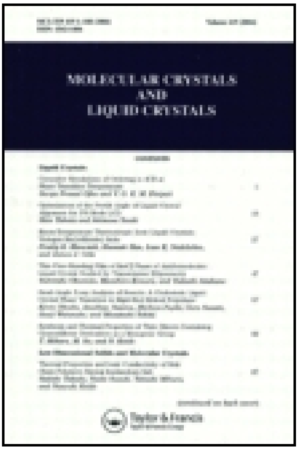

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Occurrence of Reentrant Nematic and Reentrant Smectic A Phases in Mesogenic Series

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Occurrence of Reentrant Nematic and Reentrant Smectic A Phases in Mesogenic Series

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A systematic comparative study of several series of chemically neighbouring compounds apt to give a reentrant mesomorphism is proposed. Experimental data concerning the various reentrant phases are summed up. From these observations various factors favourable to the occurence of the reentrance are revealed. Thus, the chemical composition, the sense and the location of dipoles in the molecules, the reduced temperatures, the length of the rigid core are discussed as relevant parameters.

INTRODUCTION

The reentrant nematic is one of the most novel phenomenon reported these last years in the phase transitions in liquid crystals. Indeed, it concerns the reappearance, after passing through a smectic A phase, of a nematic phase of higher symmetry than a S_A phase by lowering the temperature (or by increasing pressure). In the field of condensed state physics, this type of transition has been only observed for superconductors[1-4] and in the case of the He^3 melting.[5] Since the prime discovery in liquid crystals by P. E. Cladis,[6] rather numerous works have been performed either on mixtures[7-10] or with pure compounds at high pressure.[11-13] Among these ones, X-Ray diffraction studies[8,9,14,15] have provided some information about the nature of reentrant nematic phases which is somewhat incomplete due to the metastability of the reentrant nematic or to the complexity of the multi-components systems. Nevertheless, it emerges mainly from these studies that the reentrant structure is similar to the "classical" nematic one. Moreover, it appears necessary for the "reentrant" compound to generate, in the S_A phases, layers the thickness of which, d, is larger than the molecular length, l. in its most extended form ($d/l \simeq 1.3, 1.4$). This structure is generally obtained with molecules involving a strong dipolar end group[16–21] and, up to now, only cyano derivatives have given reentrant phases. These experimental observations lead the authors to suggest a partial head to tail overlapping of the molecules and a reentrant model is proposed[11,13] in which the dipolar interactions are challenged by steric repulsions. The interpretation in terms of a Landau theory which resumes the arguments of an optimum density for S_A phase stabilization,[22] properly describes the phenomenon but gives no account of the microscopic arrangement model previously mentioned. However, this theory as well as thermodynamical arguments[23–25] emphasize the non-pathological character of the reentrance and specify the thermodynamical conditions for its occurrence.

The discovery of the first pure compound exhibiting a stable reentrant nematic at atmospheric pressure[26] gave a new stimulus to the knowledge of the reentrant phases. Moreover, the existence at lower temperature of an additional S_A phase was shown.[27] This phase was identified to the higher S_A by miscibility diagrams[28] and its nature supported by X-Ray experiments.[29,30] Thus, a new polymorphism with isotropic-nematic-smectic A-reentrant nematic-reentrant smectic A phases was revealed in a pure compound: the octyloxybenzoyloxy cyanostilbene.[32]

This stabilization of reentrant phases at 1 atm enabled us to get much information about their structures peculiarly concerning the low temperature S_A phase for which some characteristics are very singular.[29] The measurement of viscoelastic parameters[6,27,31] such as the twist viscosity γ_1 are of course largely facilitated by the thermal stability of the reentrant nematic and its behavior in this phase is somewhat unusual due to the presence of the two smectic A phases.[27]

As a matter of course, from the skeleton of the previous molecule with slight changes, numerous other compounds were synthetized afterwards giving also reentrant phases at $P = 1$ atm. In particular, we have made progress in a study centered on the synthesis of various compounds in which the polarity and the structure are not randomly modified but keep some common features with our original compound exhibiting two reentrant phases. In this manner, we can define some factors favourable to the reentrance concerning the chemical structure as well as the physical parameters (chemical functions, layer spacing, sense of the dipoles and so on).

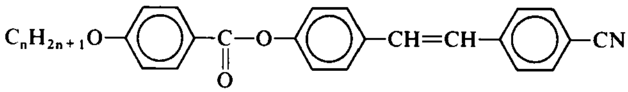
EXPERIMENTAL RESULTS

We analyse in this study a series of compounds most of which are synthetized in our laboratory, but we refer also to some series recently published elsewhere. In this section, we describe the known physical characteristics of these various substances.

1 Alkoxybenzoyloxy cyanostilbene compounds[32]

This series is the oldest known[26,28] to present stable reentrant phases, thus different observations are yet performed. They are summarized here after. As it will be done for each family we list the polymorphism of the various homologues (Table I).

TABLE I[28]



n	K		S_A		N		S_A		N		I
4	-	106	-	151	—		—		-	318	-
5	-	103	-	153	—		—		-	321	-
6	-	100.5	-	143.5	—		—		-	310	-
7	-	99	-	127	—		—		-	293	-
8	-	95.5	-	[94.1]	-	137.8	-	248.5	-	282.8	-
9	-	97	-	[63]	-	93.7	-	261	-	275.3	-
10	-	96.5	—		-	[77.9]	-	265.4	-	270.4	-
12	-	98	—		—		-	258	-		-

[] monotropic transition.
- the phase exists
— the phase does not exist

The X-Ray diffraction study[29] of the mesophases of the $n = 8$ compound has confirmed the reported polymorphism deduced from microscopic observations (including contact method experiments) and also from additional measurement of the dynamic twist viscosity coefficient in the reentrant nematic or of the magnetic anisotropy in the smectic A phases.[27] In addition, the X-Ray patterns have provided important details about the thermal evolution of the structure:

In the "high temperature" S_A phase, the layer spacing decreases with temperature. The d/l ratio (d: layer spacing, l: length of the stretched molecule) varies from 1.24 at 250°C to 1.11 at 140°C. In the "low temperature" S_A phase d is almost constant and equals one molecular length. Moreover, the diffuse scatterings which appear in these patterns and which can be assigned as satellites to the fundamental periodicity, indicate the existence of a substructure which extends perpendicular to the layers and in a parallel direction. A tentative representation is depicted in Figure 1.

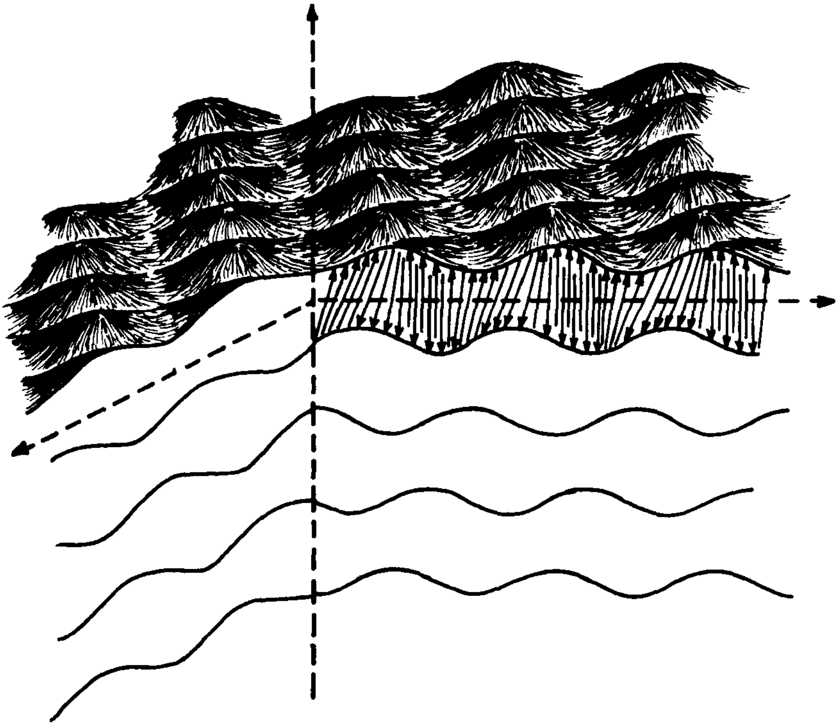


FIGURE 1 Tentative representation of the two dimensional superlattice of the reentrant S_A phase of the octyloxybenzoyloxycyanostilbene. The periodicity of undulations is about 70 Å in the layer plane. The periodicity in the director direction (i.e. perpendicular to the layers) is approximately 4 layer spacings (120 Å).

For the lower homologues of this series (without reentrant phases), the X-ray investigations have shown that the S_A phase possesses a d/l ratio $\simeq 1$, with no apparent temperature dependence and the patterns revealed singular diffuse scatterings as described above. At last, in the nematic phase of the compounds with $n \leq 7$, the d/l ratio (determined for the cybotactic groups) increases with T; this is an unusual behavior which seems to denote a gradual evolution of the "pair" associations (size or number of "dimers"?) in the nematic phase.

On the other hand, with $n \geq 8$ it is important to note that the two smectic A phases (at low and high temperature) of a given compound are isomorphous (Figure 2) (contact method as well as DSC measurements) and thus this validates the reentrant nature of the low temperature S_A phase.

In addition, P. E. Cladis has performed a high pressure experiment on the $n = 8$ compound.[33] The resulting thermobarogram indicates an unusual

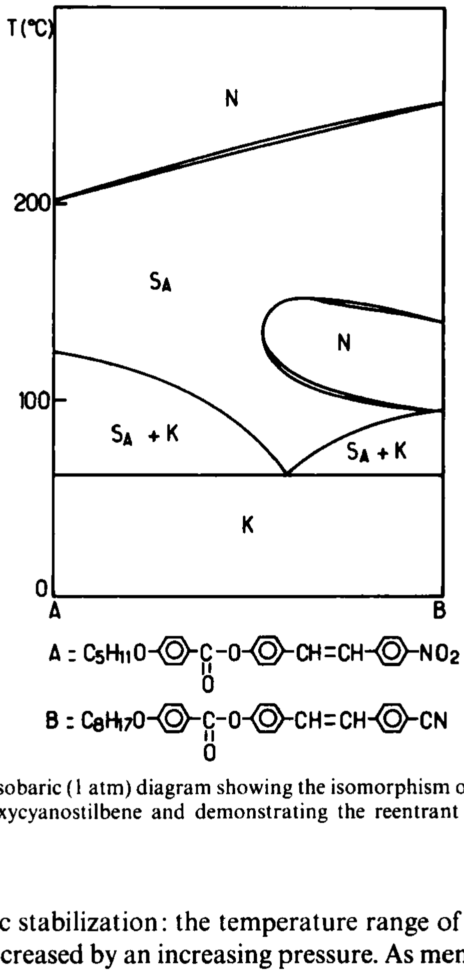


FIGURE 2 Binary isobaric (1 atm) diagram showing the isomorphism of the two S_A phases of the octyloxybenzoyloxycyanostilbene and demonstrating the reentrant character of the low temperature S_A.

feature for smectic stabilization: the temperature range of the low temperature S_A phase is increased by an increasing pressure. As mentioned elsewhere, the studies of the $n = 8$ compound suggest that the reentrant nematic can be the consequence of a competition between two S_A phases of the same macroscopic symmetry but with different short-range order. Considering the S_A character of both smectics it is thermodynamically possible that for one compound, the three N-S_A transitions belong to a same phase boundary, as proposed by us[26] and after detailed by other authors.[33,34] Up to now, we are unable to prove the continuity of such a line because the S_A domains remain always separated by a nematic phase in the successive diagrams drawn with the members of this cyano stilbene series (Figure 3). The high pressure (P.T.) diagram of the $n = 8$ homologue fails to give evidence for this continuity because one would have to consider negative pressures lower than 1 atm.

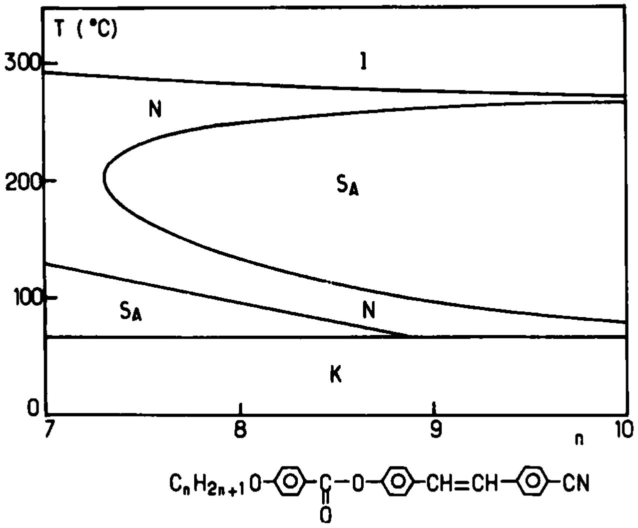


FIGURE 3 Juxtaposition of the successive isobaric (1 atm) binary diagrams between homologues of the alkoxybenzoyloxycyanostilbene series.

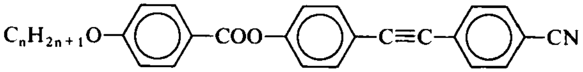
We can note that, referring to the analogy between the normal-superconductor transition and the N-S_A system proposed a few years ago by De Gennes,[35] the continuity of the N-S_A phase boundary would support theoretical considerations built up for superconducting alloys with Kondo impurities.[3] These predict for certain concentrations of impurities the existence of three transitions in a part of the temperature-concentration diagram.[36] Nevertheless, contrary to the N-S_A system, the third critical temperature corresponding to the reentrant normal-reentrant superconductor transition has not been experimentally revealed yet to our knowledge.

By comparison with the data collected in this series we shall intend to specify in the description of the following series the more or less favourable factors for reentrance.

2 Alkoxy and alkyl benzoyloxy cyano tolane compounds[37]

The tolane linkage has been introduced in order to lower the transition temperatures with respect to the cyano stilbenes. Table II shows that this effect is achieved for the N-I and high temperature N-S_A transitions (when several N-S_A transitions are observed). On the other hand, for a given length of the aliphatic chain, the other N-S_A transition temperatures are enhanced when reentrance occurs. However, in this series, the temperature of maximum

TABLE II[37]



n	K		S_A		N		S_A		N		I
5	-	107	-	[104.7]	—		—		-	276	-
6	-	113	-	[107]	—		—		·	268	-
7	-	102	-	108	—		—		-	256	-
8	-	86	-	96	—		—		-	248	-
9	-	90	-	[75.7]	-	141	-	183	-	239	-
10	-	84	—		-	102	-	208	-	233.5	-
11	-	85	—		—		-	213	-	227	-
12	-	92.5	—		—		-	216	-	223	-

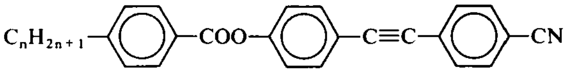
stability of the low temperature S_A phase is reduced by comparison with the stilbene series.

Let us note that the isomorphism of the various phases of this series has been supported by identification with the $n = 8$ compound of the first series.

Further, the d/l ratio of the $n = 10$ alkoxy compound seems constant in the S_A phase at a value of 1.25.

In the case of the alkylbenzoyloxycyanotolanes (Table III)[38] the temperatures are also lowered but as reported yet for the two phenyl rings compounds,[13] the substitution of an alkyl to an alkoxy chain interferes with the occurrence of the nematic reentrant phase. Moreover the alkyl group destabilizes strongly the low temperature S_A phase: for short chains, this phase appears monotropic succeeding to very large nematic ranges and for long chains ($n \geq 10$) it is impossible to detect a reentrant S_A phase.

TABLE III[38]



n	K		S_A		N		S_A		N		I
5	-	115	—		—		—		-	258	-
6	-	100	-	[78.5]	—		—		-	242	-
7	-	87	-	[63]	—		—		-	234	-
8	-	78	-	[53]	—		—		-	228	-
9	-	71	-	[44.5]	—		—		-	227	-
10	-	65	—		-	[62]	-	188	-	217	-

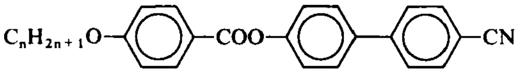
3 Alkoxy benzoyloxy cyano biphenyl compounds[39]

The modification which corresponds to elimination of the stilbene or tolan linkage is not very damaging to the reentrant nematic although all the transition temperatures are clearly lowered (Table IV)

At the opposite, the low temperature S_A phase has disappeared. The X-Ray investigations of the $n = 8$ homologue could explain this fact. First, the d/l ratio is constant ($\simeq 1.17$) in the high temperature S_A phase which differs from the behaviour of cyanostilbenes (see Section 1) and as for the $n = 10$ alkoxytolane derivative this difference can be the consequence of a larger distance from an hypothetical smectic phase at still lower temperature. In addition, the X-Ray patterns of the reentrant nematic phase obtained at low temperature reveal diffuse spots which remind of "skewed cybotactic groups" of S_C type.[40]

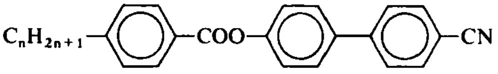
In this case too, the substitution of an alkyl chain to the alkoxy one rules out the reentrant phenomenon in the pure compounds (Table V), but a mixture of the $n = 7$ and $n = 8$ homologues indicates that these molecules

TABLE IV[39]



n	K		N		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 V



n	K		S_A		N		I
7	-	89	—		-	224	-
8	-	70	-	184	-	217	-
9	-	63	-	197	-	212	-
10	-	88	-	199	-	205	-

Note: a mixture of the n = 7 and n = 8 compounds induces reentrant phases (cf. 6).

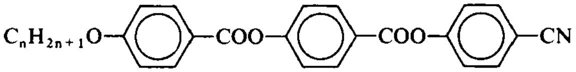
are also apt to give the reentrance. Such hidden reentrance is discussed further here (see 6).

4 Alkoxy benzoyloxy benzoate of cyanophenyl compounds

There exists a reentrant nematic in this series too,[41] but only in a monotropic state. No reentrant S_A phase occurs (Table VI).

The second benzoate linkage tends to lower transition temperatures but unfortunately with the vanishing of reentrant phases.

TABLE VI



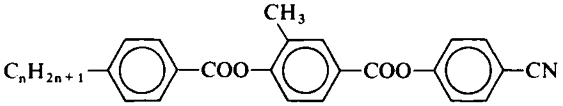
n	K		N		S_A		N		I
8	-	116	—		—		-	229	-
9	-	121	-	[116]	-	198	-	228.5	-
10	-	108	-	[94.5]	-	208	-	222	

5 Other compounds with reentrant phases

Various other cyano derivatives including the three phenyl rings skeleton are now reported. We have summed up their main characteristics in this section.

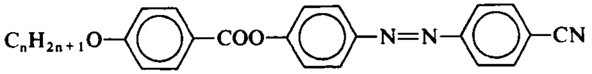
a) Cyanobiphenyl-3-methyl-4-(alkyl benzoyloxy) benzoates[42] For these compounds (Table VII) the transition temperatures are rather low but the reentrant nematic is always monotropic and arises far from the melting point. This confirms the destabilizing character of the alkyl chains. It is also

TABLE VII[42]



n	K		N		S_A		N		I
11	-	103	-	[78.5]	-	127	-	152.5	-
12	-	102	-	[59.8]	-	138.5	-	148	-

TABLE VIII[46]



n	K		S_A		N		S_A		N		I
2	-	147	—		—		—		-	334	-
3	-	113	-	[83]	—		—		-	318	-
4	-	112	-	[109]	—		—		-	297	-
5	-	99.5	-	123	—		—		-	285	-
6	-	108	-	124	—		—		-	277	-
7	-	103.5	-	120	—		—		-	269	-
8	-	93	-	98	—		—		-	259	-
9	-	88.5	-	[69.5]	-	116	-	214	-	251	-
10	-	102	—		-	[94.5]	-	225	-	245	-
11	-	99	—		—		-	230	-	240	
12	-	93	—		—		-	231	-	234	-

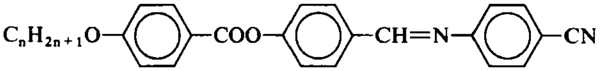
obvious that the methyl substituent on the middle phenyl ring plays a role in the non-existence of the reentrant S_A.

Despite the metastability of the reentrant phase, several physical measurements were achieved using these compounds.[43–45]

b) *Alkoxybenzoyloxy-4′-cyanoazobenzene*[46] The general features of these compounds (Table VIII) are close to these of the cyanostilbene series (see Section 1). But the maximum stability of the low temperature S_A phase is observed at 124°C for the *n* = 6 compound, lower than for the stilbene series (153°C, *n* = 5, see Table I) and this causes a greater metastability of this phase when it becomes reentrant (*n* = 9).

c) *Alkoxybenzoyloxy-4′-benzilidene-4-cyanoanilines*[47] An enantiotropic reentrant nematic is reported for the *n* = 8 compound and from *n* = 9 this

TABLE IX[47]

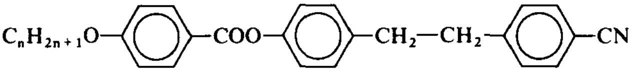


n	K		S_A		N		S_A		N		I
6	-	113.5	-	[91]	—		—		-	274.5	-
7	-	114.5	-	[70]	—		—		-	263.5	-
8	-	107.5	—		-	153	-	197.5	-	255	-
9	-	96	—		-	[92]	-	228	-	251	-

phase is monotropic. The low temperature S_A phase exists monotropic with the lower homologues ($n = 6,7$) but it does not remain as reentrant S_A phase for the $n = 8,9$ compounds. Thus, the N-S_A-N-S_A "tetramorphism" is absent in this series (Table IX).

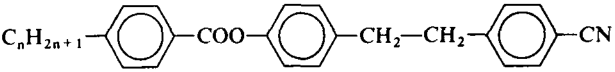
d) Alkoxy or alkyl benzoyloxyphenylcyanophenyl ethanes[48] In these series (Tables X and XI) the difference lies in the disrupted conjugation between two phenyl rings which produces a large increase of the flexibility. The nematic-isotropic transition temperatures are fairly low but without reentrant phase in the pure compounds of the alkoxy series. Indeed, we point out that, unusually, no S_A phase appears with the alkoxy chain even for $n = 8$ whereas the $n = 8$ alkyl compound presents stable S_A. A virtual reentrant nematic has been recently predicted[47] in this latter compound from binary diagrams constituted with the Schiff bases of the Table IX. This tendency has

TABLE X



n	K		N		I
1	-	168	-	199	-
2	-	144	-	199	-
4	-	108	-	185	-
7	-	83	-	169	-
8	-	85	-	166	-

TABLE XI



n	K		S_A		N		I
3	-	115	—		-	166	-
5	-	121	—		-	158	-
6	-	100.5	—		-	150	-
7	-	89	—		-	150	-
8	-	92	-	96	-	144	-

Note: a monotropic transition to a very metastable reentrant nematic has been observed by the droplet technique for the $n = 8$ homologue.

been confirmed by the observation of a monotropic transition by the droplet technique.

6 Series with virtual reentrant phases

For reasons of greater stability of the crystalline phase than the reentrant nematic, this latter is often unobservable even in a metastable state. Nevertheless as we above remarked see 3 and 5, the binary diagram technique allows to determine if a given compound is apt to give the reentrance in mixtures (Figure 4). Moreover, in this way we can evaluate a "virtual" temperature of reentrant nematic transition for the pure compound. The series of the Table V, yet mentioned, and the following ones are in this case.

a) 4'-alkoxybenzoyloxy-4-cyano-α-cyanostilbene[48] Now, we change markedly the electronic distribution (the molecular dipole deviates from the average molecular axis) and also the molecular hindrance. As consequence we see the disappearance of reentrant nematic and smectic phases (Table XII) in the pure compounds. But a contact method gives evidence for a reentrant nematic domain in the binary diagram of the two successive homologues with $n = 8$ and $n = 9$ and a virtual transition can thus be proposed for this last one.

b) Alkoxybiphenyl carboxylates of cyanophenyl The cyano end group is kept and if we compare to the compounds in the Table IV (which give a

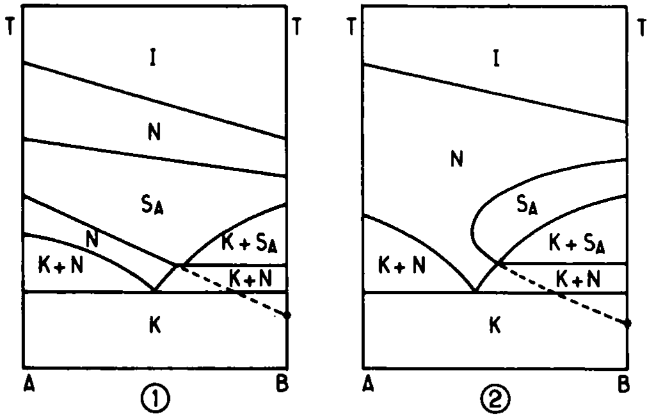
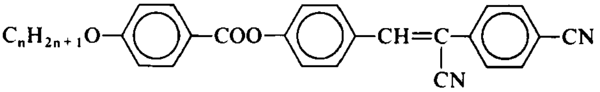


FIGURE 4 Schematic diagrams indicative of a reentrant tendency for the compound B (a) binary diagram with a compound exhibiting a stable reentrant nematic (b) binary diagram with a compound without stable reentrant phase.

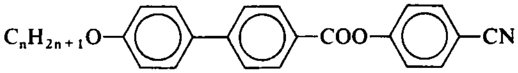
TABLE XII



n	K		S_A		N		I
4	-	149	—		-	270	-
7	-	133.5	—		-	242	-
8	-	133	—		-	238	-
9	-	133	-	209	-	233	-
10	-	130	-	214	-	224	-

reentrant nematic) the two linkage groups between the three phenyl rings are simply inverted. Although these materials do not exhibit a reentrant phase; (Table XIII), a virtual reentrant nematic is expected since the binary diagram with $n = 8$ and $n = 9$ compounds reveals a domain of reentrant nematic.

TABLE XIII



n	K		S_A		N		I
8	-	114	—		-	227.5	-
9	-	118	-	197	-	221	-

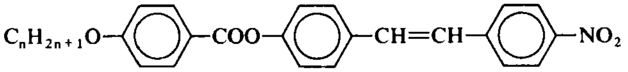
7 Series without reentrant phases

Within the series above listed at least one member exhibits a stable, a monotropic or a virtual reentrant phase. This can seem not so surprising if we consider their similar structures. We shall now take interest in some other chemically neighbouring series which, however, do not induce reentrant phases.

a) Alkoxybenzoyloxynitrostilbene If we compare to the cyanostilbene (see Section 1) only the size of the terminal group, more hindering, changes. Nevertheless the reentrant phases are withdrawn (Table XIV).

The X-ray study of the $n = 5$ compound has revealed an interlayer spacing in the S_A phase practically equal to one molecular length. Moreover, no diffuse scattering like these described with the cyanostilbenes (see Section 1) or the cyanobiphenyls (see Section 3), appear. This seems to indicate

TABLE XIV

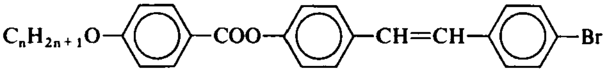


n	K		S_A		N		I
3	-	150	—		-	>290	-
4	-	127			-	>280	-
5	-	124	-	201	-	>280	-
6	-	123	-	236	-	>280	-
7	-	99	-	265	-	287	-
8	-	100	-	271	-	281	-
9	-	97	-	274	-	277	-
10	-	99	-	274	—		-
11	-	101	-	273	—		-
12	-	100	-	270	—		-

that this S_A phase with $d/l \simeq 1$ is not as the low temperature S_A phase of the cyanostilbene series. The fact that the structure is not at all "bilayer" appears nevertheless unexpected because layer spacing larger than one molecular length has been reported for compounds with two phenyl rings and a nitro end group.[20,21,49] On the other hand, such compounds are not able to generate reentrant nematic phases even at very high pressures.[49] In addition, the continuous and regular evolution of the N-S_A transition temperature throughout this nitro series denotes a "classical" behavior of the smectic phase in terms of McMillan's criteria (see II). At last, it is important to remark that the S_A phase of the $n = 5$ nitro compound is isomorphous to the *two* S_A phases of the $n = 8$ cyanostilbene (Figure 2).

b) Alkoxybenzoyloxybromostilbene[38] In the compounds of the Table XV the terminal polar group is now a bromine. This atom is much more hindering

TABLE XV[38]

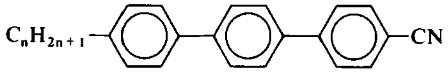


n	K		S_B		S_A		N		-
1	-	176	-	[166]	—		-	>310	-
4	-	150	-	153	-	229	-	295	-
7	-	114	-	144	-	230	-	251	-
8	-	113	-	146	-	257	-	267	-

with less polarity than cyano or nitro group. No reentrant phase occurs, but "ordered" smectic B phases arise as usually with bromo derivatives.[48]

c) *Alkyl-p-cyanoterphenyls* G. W. GRAY *et al.*[50] have not observed reentrant phases for such compounds but have observed ordered smectic phases for the $n = 8$ homologue (Table XVI).[51]

TABLE XVI[51]



n	K		S_E		S_B		S_A		N		I
3	-	182	—		—		—		-	257.5	-
5	-	130	—		—		—		-	239	-
6	-	125	—		—		—		-	228	-
7	-	134	—		—		-	[125.5]	-	222	-
8	-	127	-	128	-	133	-	197	-	216	-

Few compounds with a terminal cyano group give one or several ordered smectic phases.[52] We have previously indicated that the withdrawing of the linkage group between phenyl rings located in α position with respect to the cyano group does not suppress the reentant nematic (see Section 3: Table IV). Furthermore, replacing alkoxy chain by an alkyl chain, the reentrant nematic is destabilized but no ordered phase is induced (see Section 3: Table V). Thus, to cancel the COO linkage situated on the aliphatic-tail side could play an important role in the radical change of the polymorphism.

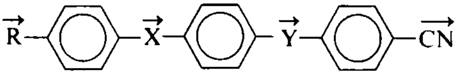
In fact, it would be interesting for the compounds listed in the Table XV to control that the reentrant phenomenon is not concealed by a greater stability of the ordered smectic phases and if virtual transitions to reentrant phases are possible.

DISCUSSION

The mesomorphous reentrant phenomenon at atmospheric pressure is gradually losing its pathological character since several series and numerous compounds are known at present to exhibit nematic and/or smectic A reentrant phases. Moreover, from the study of these families there emerge some common features in favour of the occurrence of a reentrant phase.

Concerning the chemical scheme of the molecule it is clear that the cyano end group seems essential. This seems to be the consequence of a very strong dipole connected with relatively small dimensions. By comparison, the molecules with a terminal NO_2 group (which possesses quite the same dipole but a higher hindrance), seem not to be so suitable to give reentrant phases.

The electronic distribution along the molecule seems also to have an effect. The conjugation of the overall rigid core appears highly favourable when it takes place in such a way that the maximum electronic density is located on the CN group, the positive site being on the rigid core at the farthest extremity from the nitrile. For short, a single sense for the transmission of the electronic effect seems consistent as following depicts:



Note that the inverted $\overleftarrow{X}$ or $\overleftarrow{Y}$ dipole cases have not been yet considered. Some additional remarks about the chemical structure can be put forward:

—it seems better but not absolutely necessary (see Ref. 42) for the rigid core to involve at least three benzenic rings.

—an alkoxy chain is generally always more favourable to the reentrance than an alkyl chain.

—at last, we cannot claim that X = COO is essential although it appears in most studied series (generally by reason of easier synthesis). In this case the comparison of the various series allows to classify the different "*Y*" linkages with regard to their capacity to stabilize reentrant phases in pure compounds:

$$\mathrm{CH{=}CH} > \underset{\mathrm{C{\equiv}C}}{\mathrm{N{=}N}} > \underset{\text{nothing}}{\mathrm{CH{=}N}} > \mathrm{COO} > \mathrm{CH_2{-}CH_2} > \mathrm{CH{=}CCN}$$

For the "best" groups the reentrant phases are thermodynamically stable, being metastable from COO group and eventually virtual for the CH=CCN one.

But other factors appear as relevant as the chemical characteristics for the observation of reentrant phases at atmospheric pressure.

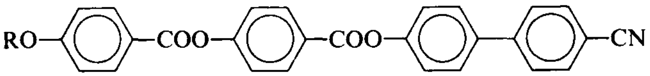
In the N-S_A-N-S_A sequence, the two S_A phases are distinct at the short range order but we can find macroscopic parameters sensitive to this difference. For example, the evolution of the T_{NA}/T_{NI} ratio (T_{NA}:higher transition temperature between a nematic and a smectic A, T_{NI}: nematic-isotropic transition temperature) for the successive homologues is not continuous. In the cyanostilbene series (see Section 1), this ratio remains almost constant and lower than the McMillan's number $(0.87)^{53}$ up to $n = 7$.

Then it rises dramatically for $n = 8$ as a consequence of the insertion of the high temperature S_A phase (Table XVII). In contrast, we note that the entropy excess at the N-S_A transitions is as weak for the high temperature S_A phase as for the low temperature one.

TABLE XVII

n	4	5	6	7	8	9	10
T_{NA}/T_{NI}	0.72	0.71	0.71	0.70	0.93	0.97	0.98

A geometrical factor can be efficient: the conjugated part length for isometric chains. For molecules with two phenyl rings, the core is relatively short (typical 10–15 Å) the reentrance is hence obtained only at high pressure and at rather low temperatures. In the case of three phenyl rings the core size is about 20 Å. Reentrant phases are stable at atmospheric pressure but the transition temperatures are elevated. On the basis of these facts we can propose some assumptions. The evolution of the nematic to smectic A phase lines could be understood as represented in the Figure 4: in a P, T, l_c (length of the conjugated part of the molecule) diagram, sections of different l_c value are considered. The experimental curves can be drawn: the first one in the plane POT corresponding arbitrarily to $l_c = 13.5$ Å length of the octyloxycyanobiphenyl core (the "virtual" lower transition temperature at about 12°C is extrapolated from results of references[11,13] and from the fitting of reference 22). The second one in a plane $l_c = 22$ Å, length of the rigid core of the octyloxybenzoyloxycyanostilbene. The $l_c = 26.5$ Å plane is relative to the following compound:



for which only one N-S_A transition occurs at $T \simeq 337$°C for $P = 1$ atm. (the S_A phase remains in a large temperature range). The point takes place approximately on a straight line drawn from the higher N-S_A transition temperatures of 8OCB and cyanostilbene. We can suggest that in this case no reentrant phase is observable because the whole phase line lies above the atmospheric pressure as depicted in the Figure 4. But a slight increase of the pressure should be sufficient to reveal reentrant nematic and smectic A phases... For the compound

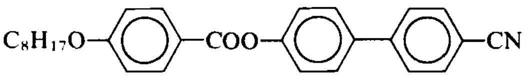
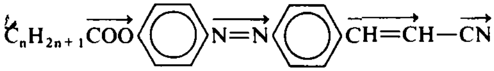


TABLE XVIII[55]



n	K		S_A		N	S_A		N		I	$\frac{T_{NA}}{T_{NI}}$
1	-	164.9	-	182.3	—	—		-	252.2	-	0.87
2	-	166.1	—		—	—		-	251.5	-	
3	-	104	-	159.8	—	—		-	235.1	-	0.85
4	-	97	-	142	—	—		-	221	-	0.84
5	-	84.5	-	125	—	—		-	216.5	-	0.81
7	-	80	—		?	-	164	-	199.7	-	0.92
8	-	83.5	—		—	-	182	-	195.8	-	0.97
9	-	86	—		—	-	186.6	-	191.1	-	0.99

We have resumed the data of Titov *et al.*[55] Although they have not specified the character of the smectic modification phase, we suggest that it is a smectic A phase.

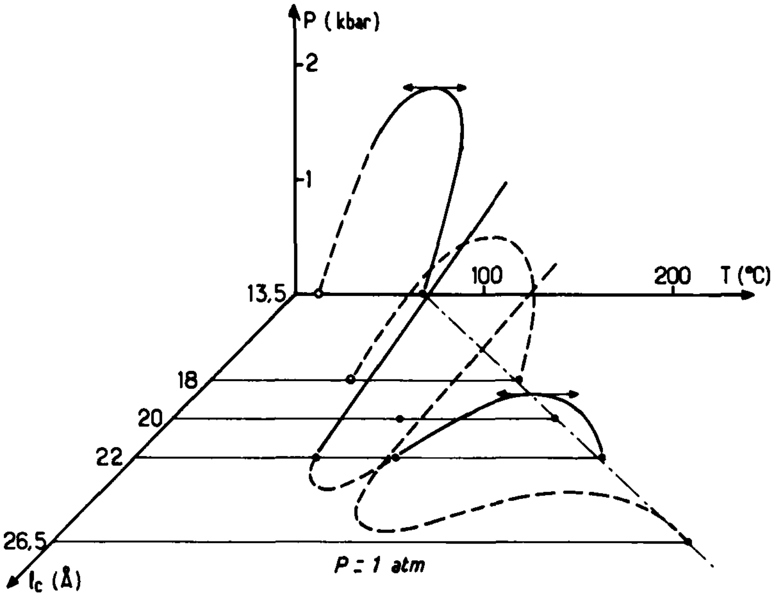


FIGURE 5 Tentative representation of the evolution of the N-S_A boundaries in a P, T, l_c space. l_c: length of the conjugated part of the different molecules with constant number of carbons (8) in the chain. Full lines and points in the 1 atm. plane: experimental results. Dotted lines = assumed shapes of other N-S_A phase lines.

the length of the rigid core is 20 Å (instead of 22 Å for stilbene linkage), and a linear evolution of the higher N-S_A transition temperature with respect to the length of the conjugated part is corroborated (see Figure 4). In contrast. no simple correlation can be proposed for the lower transition temperature (we remind that the X-ray studies have shown a somewhat different behaviour of the local order of the S_A and reentrant nematic phases of this biphenyl compound by comparison with the compounds of the stilbene series (see Section 3).

These few examples seem to support the important role of the conjugated part length. Moreover, this argument is more favourable to a model assuming an equilibrium[54] between the monomer and a dimer form with a complete overlapping of the rigid cores[11,18,19] (such as the average d/l value is in the (1.0, 1.3) range) than to a model of a partial and gradual overlapping of all the molecules which cannot explain the relevance of the l_c parameter.

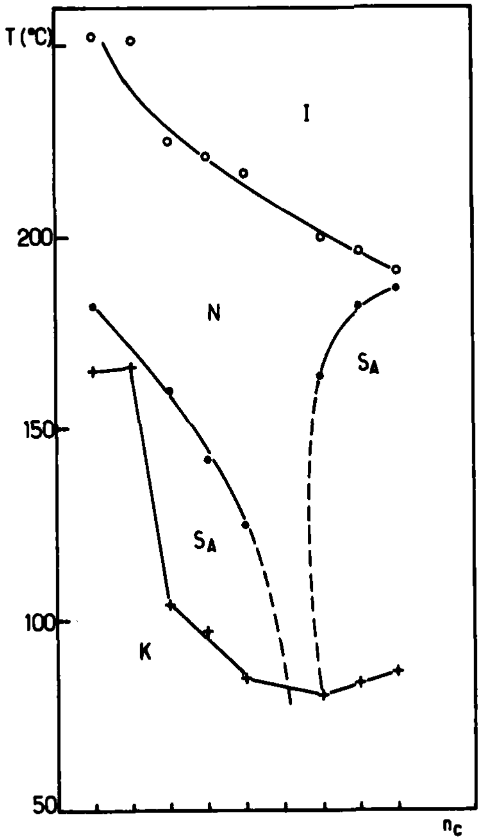


FIGURE 6 Diagrammatic representation (T = temperature, n_c = number of carbons in the chain) of Table XVIII. The dotted lines define the supposed reentrant nematic domain.

At last, we have yet indicated that the reexamination of formerly studied series (at $P = 1$ atm.) would yield evidence for reentrant phases (unexpected because monotropic or assimilated to other mesophases).[39] For example, let us consider the features of the series reported in the Table XVIII in order to make more precise the provisional character of our approach.

The chemical constitution of such molecules seems consistent with reentrance. Moreover, the evolution of the various transition temperatures versus the number of carbon of the chain recalls series giving reentrant phases. This is illustrated in Figure 5 but also by the variation of the T_{NA}/T_{NI} parameter which increases suddenly for $n = 7$. If we consider the $l_c = 18$ Å plane (corresponding to the conjugated part of this series) in the Figure 4, we can remark that the N-S_A transitions would be 163°C (highest transition) and 76°C (S_A-reentrant nematic). The $n = 7$ homologue of the Table XVIII series (for which the R COO chain is isometric to the $n = 8$ compounds with RO chains considered in the Figure 4) presents a N-S transition at 164°C. Thus, in our point of view, (referring to the melting point of the $n = 7$ homologue $T_{K\rightarrow S} \simeq 80°C$) the reentrant phase would be expected monotropic or at least virtual which could explain why it was not reported....

To conclude, we emphasize that in this paper we have restricted our study to the reentrance with regard to the molecular structure. In a forthcoming paper we shall present a more general study of these very stimulating long polar derivatives including other phenomena dealing with the molecular polarity such as S_{A_1}-S_{A_2} transitions.[56,57] This will make a pair of the theoretical comprehensive view of the smectic A phase discussing these various polar effects built up by J. Prost.[58]

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