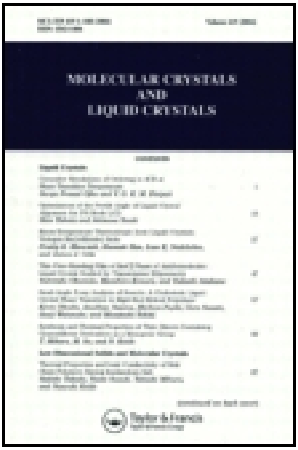

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Molecular Aspect and Polymorphism in Polar Rod-Like Mesogens

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MOLECULAR ASPECT AND POLYMORPHISM IN POLAR ROD-LIKE MESOGENS

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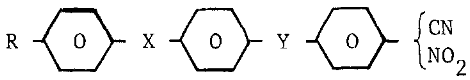
Abstract Strongly polar molecules with the general formula :

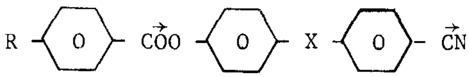


show a great variety of interesting polymorphism such as reentrant phases and some new smectic phases. The importance of the relative longitudinal dipolar moment of the cyano or nitro group and of the different X and Y linkages has been clearly underlined. For this purpose four families of polar mesogens belonging to the above structure with X, Y = – COO –, – CH = N –, – OCO –, – N = CH – have been synthesized. Some interesting results are given :

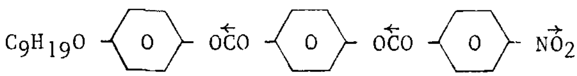
- Reentrant sequences :
  - . K S_A N_{re} S_A N I
  - . K N_{re} S_C S_A N I
  - . K S_C N_{re} S_A N I
  - . K S_A N_{re} S_C S_A N I
- Transition $S_C - S_C$
  - . K S_{C_2} S_C S_A N I
  - . K S_{C_2} $S_{\tilde{C}}$ S_C S_A N I
- Existence of different smectic A and C phases :
  - . S_{A_2} S_{A_1} S_{A_d}
  - . S_{C_2} S_{C_1} S_{C_d}

INTRODUCTION

In some previously reported papers[1,2] we have shown that the cyano compounds with three benzene rings belonging to the structure :



constitute the optimal condition for the formation of reentrant phases at atmospheric pressure. Moreover it has been already shown that the NO_2 terminal group may also lead to nematic reentrance and to new smectic phase made of ribbons[3] $S_{\tilde{C}}$ with the compound :

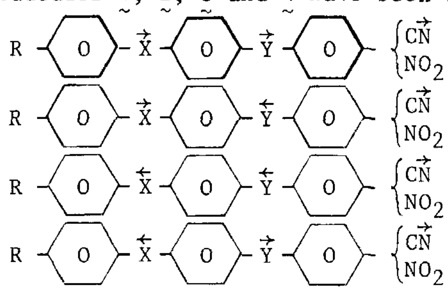


A systematic study of the influence of :

- the polar terminal group (- CN or - NO_2)
- the relative longitudinal dipolar moment of the central groups (X and Y)

on the reentrant phenomenon and the new smectic modifications was performed. For this purpose the four families of polar mesogens with three benzene rings belonging to the structures 1, 2, 3 and 4 have been synthesized :

1, 2, 3, 4



1 A {X = -COO, Y = -CH = N; B {X = -CH = N, Y = -COO

2 A {X = -COO, Y = -N = CH; B {X = -CH = N, Y = -OCO

3 A {X = -OCO, Y = -N = CH; B {X = -N = CH, Y = OCO

4 A {X = -OCO, Y = -CH = N; B {X = -N = CH, Y = -COO

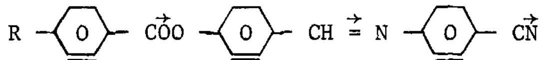
RESULTS AND DISCUSSION

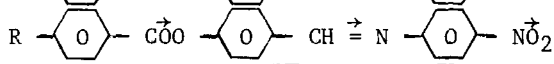
All the compounds were prepared according to well-known methods. They were purified by repeated recrystallization.

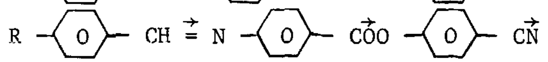
Phase transitions were studied both by polarizing microscopy equipped with a Mettler FP5 heating stage and Differential Scanning calorimetry (Dupont 990).

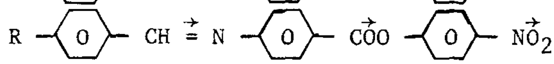
Following the longitudinal dipolar moment sense of X and Y, four families of compounds can be defined :

1. FAMILY 1 : The longitudinal dipolar moments of X, Y and CN or NO_2 are in the same sense. The four corresponding series are :

1A CN :


1A NO_2 :


1B CN :


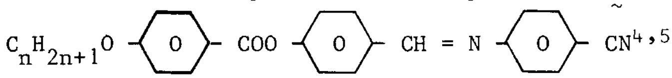
1B NO_2 :


* Series 1A CN[4,5] (Table I). In this series, three derivatives with R = $C_8H_{17}O$-, $C_9H_{19}O$- and $C_{10}H_{21}O$- exhibit a reentrant nematic phase. The latter presents for the first time the interesting sequence :

I N S_A S_C N_{re}[4]

At first, these very metastable S_C and N_{re} phases could not be identified by miscibility studies. Recently they have been proved to be miscible with those of 4-decyloxycinnamoyloxybenzylidene 4'-cyanoaniline[6], 5 (Fig. 1). In order to prove definitively these identifications, X-ray investigations were performed using an equimolar mixture of the two decyloxy derivatives in which the S_C phase is stable and the reentrant nematic phase could exist still 50°C. This study proves that the S_A and S_C are partially bilayered smectic phases[6].

TABLE I Transition temperatures of compounds of 1A CN



n	K	S_A	N_{re}	S_C	S_A	N	I
4	. 137.5	(. 101)	-	-	-	. 299	.
5	. 122	(. 102)	-	-	-	. 280	.
6	. 115	(. 91)	-	-	-	. 274	.
7	. 115	(. 70)	-	-	-	. 264	.
8	. 108	-	. 153	-	. 198	. 255	.
9	. 96	(. 40)	(. 92)	-	. 228	. 251	.
10	. 100	-	(. 66)	(. 79)	. 232	. 242	.

The meanings of the signs used in this table and in the following are :

K : crystalline phase ; N : nematic phase

S : smectic phases A, C ... , smectic phases S_A, S_C

N_{re} : reentrant nematic phase ; I : isotropic phase

. : the phase exists ; - : the phase does not exist

( ) : monotropic phase

The temperatures are given in Celsius degrees.

The metastable S_A phase observed for short chains is probably S_{A_1} because the ratio T_{NA}/T_{NI} is lower to Mc Millan parameter 0.87 (T_{NA}, T_{NI} are respectively the temperature in Kelvin of the smectic A - nematic transition at the highest temperature and the nematic - isotrope transition). From the octyloxy derivative the S_A phase is partially bilayered (S_{A_d}).

* Series 1B CN (Table II). The first seven homologues only show nematic phases. In the octyloxy and nonyloxy derivatives a reentrant nematic and S_{A_d} phases appear. The decyloxy derivative does not exhibits a N_{re} phase but it presents a

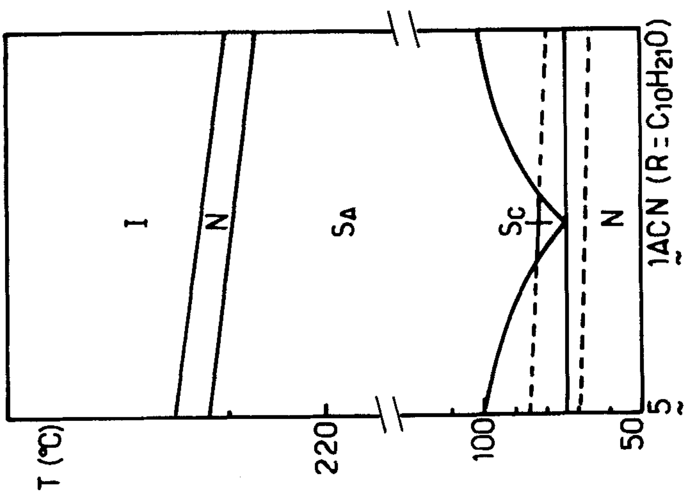


Fig. 1 : Phase diagram of mixtures

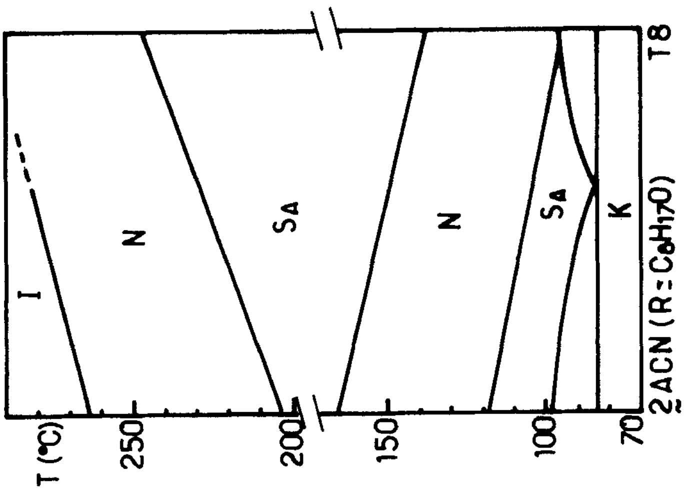
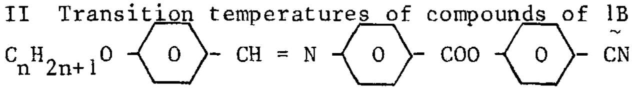


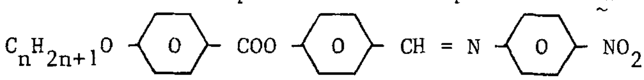
Fig. 2 : Phase diagram of mixtures

TABLE II Transition temperatures of compounds of **1B** CN



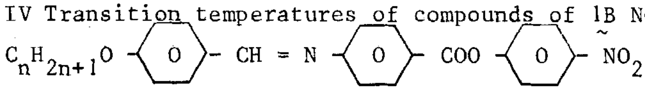
n	K		N_{re}		S_C		S_A		N		I
1	.	168	–		–		–		.	> 290	.
2	.	161	–		–		–		.	> 290	.
3	.	139	–		–		–		.	> 290	.
4	.	116	–		–		–		.	285	.
5	.	117	–		–		–		.	277	.
6	.	116	–		–		–		.	270	.
7	.	119	–		–		–		.	257	.
8	.	113	.	138	–		.	208	.	254	.
9	.	99	(.	89)	(.	84)	.	220	.	246	.
10	.	101	–		–		.	235	.	242	.
11	.	99	–		–		.	234	.	237	.
12	.	100	–		–		.	234	–		.

TABLE III Transition temperatures of compounds of **1A** NO_2 [7]



n	K		S_A		N		I
5	.	135.5	(.	117)	.	272	.
6	.	139	.	192	.	265	.
7	.	127	.	228.5	.	255	.
8	.	131	.	245	.	251	.

TABLE IV Transition temperatures of compounds of **1B** NO_2



n	K		S_A		N		I
7	.	117	.	234	.	248	.
8	.	117	.	241	.	246	.
9	.	113	.	245	–		.
10	.	117	.	244	–		.

metastable S_C phase.

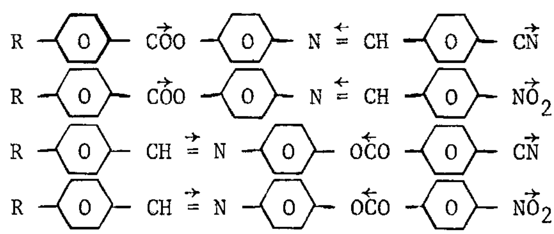
* Series 1A NO_2[7] (Table III). All the four compounds present smectic A and nematic phases. The N_{re} is not observed in this series.

* Series 1B NO_2 (Table IV). Two first compounds exhibit smectic A and nematic phases while the nonyloxy and decyloxy derivatives only present smectic A phases. In these two last series, the heptyloxy derivative only displays the high temperature nematic and S_{A_d} phases. The superior homologue octyloxy does not either exhibit a reentrant nematic phase. So it is certain that a N_{re} phase cannot be observed in the series 1 NO_2 because an increasing of the chain length is known to destabilize the S_{A_1} and N_{re} phases[1,2].

Conclusion for the family 1. Only the cyano end group gives the reentrant sequences I N S_A N_{re} and I N S_A S_C N_{re}.

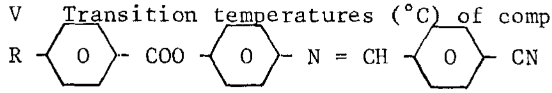
2. FAMILY 2 : The longitudinal dipolar moments of X and CN or NO_2 are in the same sense while that of Y is antiparallel. We have also four series :

2A CN :
2A NO_2 :
2B CN :
2B NO_2 :



* Series 2A CN (Table V). Twenty compounds have been synthesized with R = C_nH_{2n+1} (n = 3 → 10) and $C_nH_{2n+1}O-$ (n = 1 → 12). Up to n = 3 in these two cases, each compound has only a nematic phase. The S_A phase appears with n = 4. This S_A phase with short chain is probably a monolayered one (S_{A_1}). It presents a temperature of maximum stability with n = 6 deri-

TABLE V Transition temperatures (°C) of compounds 2A CN



R	K		S_C	S_A	N_{re}	S_A	N		I
C_3H_7	.	145	–	–	–	–	.	> 280	.
C_4H_9	.	127	–	(. 96)	–	–	.	> 280	.
C_5H_{11}	.	106	–	(. 98)	–	–	.	274	.
6_6H_{13}	.	94.5	–	. 106.5	–	–	.	262	.
C_7H_{15}	.	120	–	(. 95)	–	–	.	258	.
C_8H_{17}	.	104	–	(. 77.6)	(. 84)	. 196	.	246	.
C_9H_{19}	.	106	–	–	–	. 220	.	241	.
$C_{10}H_{21}$	.	99	–	–	–	. 227	.	235	.
CH_3O	.	160	–	–	–	–	.	> 290	.
C_2H_5O	.	134	–	–	–	–	.	> 290	.
C_3H_7O	.	130	–	–	–	–	.	> 290	.
C_4H_9O	.	117	–	(. 87)	–	–	.	> 290	.
$C_5H_{11}O$	.	101	–	. 126	–	–	.	289	.
$C_6H_{13}O$	.	104	–	. 144	–	–	.	283	.
$C_7H_{15}O$	.	104	–	. 134	–	–	.	271	.
$C_8H_{17}O$	.	98	–	. 119	. 166	. 204	.	264	.
$C_9H_{19}O$	.	113	–	(. 100)	(. 108)	. 244	.	258	.
$C_{10}H_{21}O$	.	104	–	(. 79)	(. 94)	. 245	.	254	.
$C_{11}H_{23}O$	.	88	(. 79)	–	–	. 247	.	249	.
$C_{12}H_{25}O$	.	91	(. 70)	–	–	. 247	.		.

vative (for C_nH_{2n+1} and $C_nH_{2n+1}O$). The octyloxy derivative exhibits enantiotropic reentrant N and S_A phases while the octyl, the nonyloxy and the decyloxy derivatives present monotropic reentrant N and S_A phases.

The N S_A N S_A sequence of the four compounds has been characterized first by optical textures and then checked by a contact method with a well known compound T_8[8] (Fig. 2).

The diagram of state of binary system between the decyloxy derivative and the 4(4"-decyloxybenzoyloxy)benzylidene-4'-cyanoaniline has been studied by means of the contact method and by the investigations of certain singular concentrations (Fig. 3). From this figure, we can report two important results :

- First, a new phase sequence with decreasing temperature is observed : N S_A S_C N S_A. For example, with 68.7 mol % of decyloxy derivative, the transition temperatures are :

  K 98.5 (S_A 61.2) (N 86.5) (S_C 87.5) S_A 242.5 N 251 I

- Second, we stress the existence of a rather unusual N_{re} - A - C point involving the reentrant nematic phase. This fact changes part of the topology of this point especially attractive because of its tricritical character. Unlike the "common" case (see Figures 4 and 5)[9,10] in which the sequence N $\rightarrow$ S_A $\rightarrow$ S_C is observed when one turns clock wise around the triple point, now the different sequence S_A $\rightarrow$ S_C $\rightarrow$ N_{re} is obtained. Moreover, in the previously studied systems, as depicted in Figures 4 and 5, the entropy of the N - S_C transition has been shown to decrease rapidly along the line of transition and to vanish eventually at the N - A - C point. This behavior as well as the actual shapes of the curves in the vicinity of the point of the Figure 3 have been checked[11]. We must point out that even

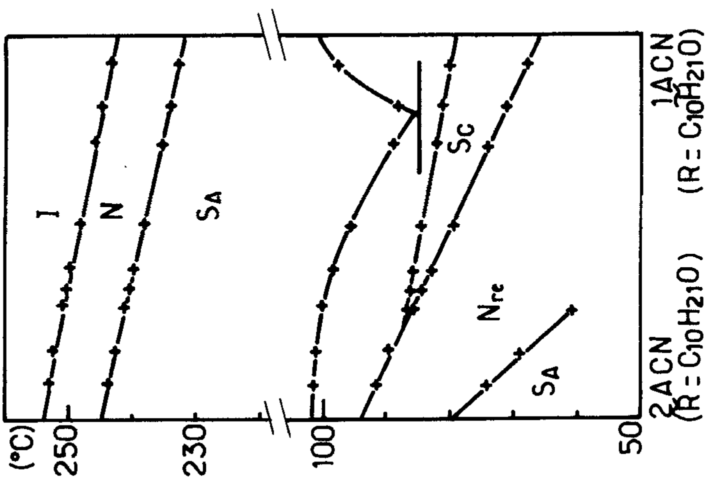


Fig. 3 : Phase diagram of mixtures

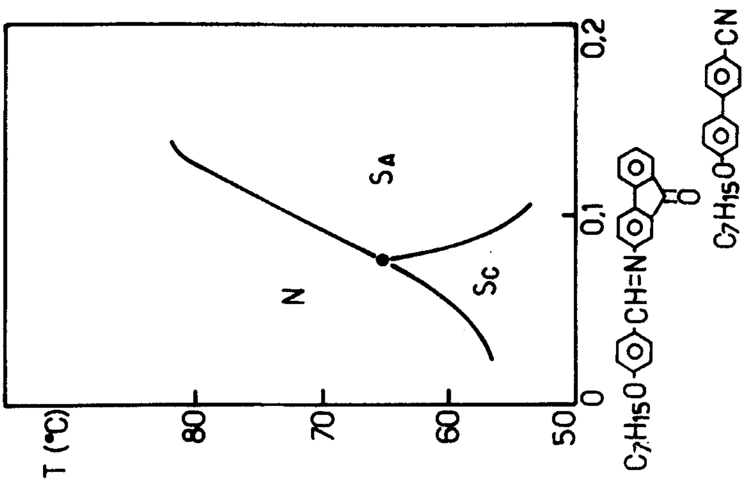


Fig. 4 : Phase diagram of mixtures

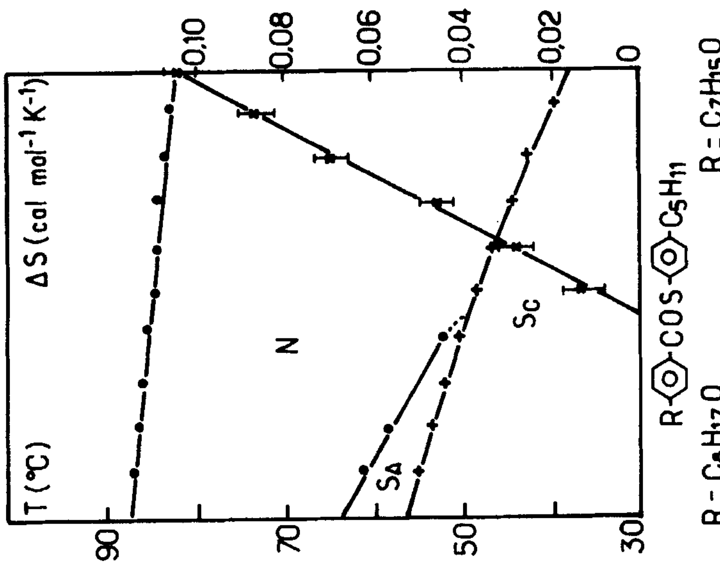


Fig. 5 : Phase diagram of mixtures

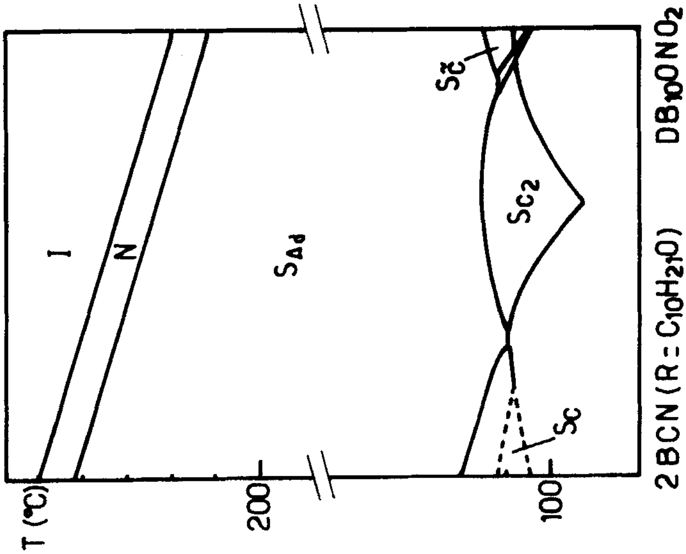


Fig. 6 : Phase diagram of mixtures

in pure compound 1A CN (R = $C_{10}H_{21}O$-) the entropy of the $S_C - N_{re}$ is very weak = 3.3 × 10^{-2} cal.mol^{-1}.K^{-1}.

* Series 2B CN (Table VI). Ten compounds of this series have been prepared with R = $C_nH_{2n+1}O$ (n = 4 → 13). The derivatives with short chain (n = 4 → 8) exhibit S_{A_1} and N phases. The nonyloxy derivative presents enantiotropic reentrant S_A and N phases. The more interesting feature is obtained with the decyloxy derivative which exhibits directly transition $S_{C_2} - S_C$ with the sequence[12] :

K S_{C_2} S_C S_A N I

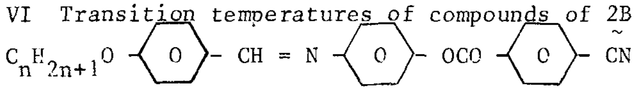
The smectic S_{C_2} phases of the four latest compounds of the series appear entirely miscible among themselves but not miscible with the high temperature S_C phase of the decyloxy derivative. The bilayer S_{C_2} nature is suggested by the phase diagram (contact method) between 2B CN (R = $C_{10}H_{21}O$) and to standard compound, $DB_{10}ONO_2$ (Fig. 6). In addition three layering reflection orders are visible in the X-ray patterns of this phase (R = $C_{13}H_{27}O$) with d ≃ 51 Å and the experimental tilt angle is large (θ > 30°) in agreement with the calculation of θ considering the expected bilayered S_{C_2} arrangement with d ≃ 2ℓ cos θ (ℓ obtained from SASM stereomodel with the completely stretched conformation (2B CN, R = $C_{13}H_{27}O$- ℓ ≃ 35 Å). The higher temperature S_A phase is a partially bilayer S_{A_d} phase with d ≃ 53 Å.

* Series 2A NO_2 (Table VII) and series 2B NO_2 (Table VIII). All eight compounds in this two series only exhibit smectic A and N phases. The N_{re} and S_C phases are not observed.

Conclusion for the family 2. In this family 2, only cyano polar end group gives :

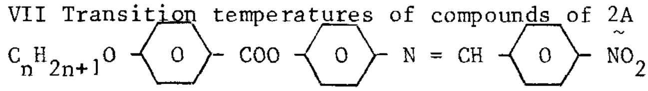
- the reentrant phenomenon with I N S_A N_{re} $S_{A_{re}}$ sequence.

TABLE VI Transition temperatures of compounds of 2B CN



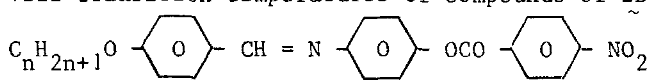
n	K	S_{C_2}	S_C	S_A	N_{re}	S_A	N	I
4	. 141	-	-	(. 136)	-	-	. > 281	.
5	. 130	-	-	. 155	-	-	. > 281	.
6	. 135	-	-	. 156	-	-	. 281	.
7	. 131	-	-	. 155	-	-	. 269	.
8	. 119	-	-	. 147	-	-	. 266	.
9	. 116	-	-	. 123	. 126	. 234	. 257	.
10	. 120	(. 106)	(. 112)	-	-	. 241	. 249	.
11	. 112	(. 102)	-	-	-	. 237	. 244	.
12	. 117	(. 113)	-	-	-	. 242	-	.
13	. 112	(. 110)	-	-	-	. 234	-	.

TABLE VII Transition temperatures of compounds of 2A NO_2



n	K	S_A	N	I
7	. 102.5	. 242	. 266	.
8	. 103	. 254	. 261	.
9	. 102	. 257	-	.
10	. 103	. 255	-	.

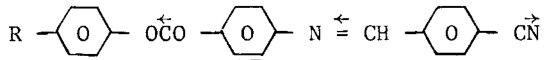
TABLE VIII Transition temperatures of compounds of 2B NO_2

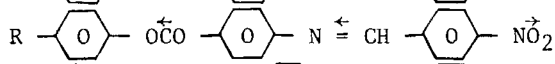


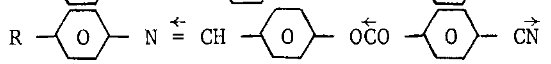
n	K	S_A	N	I
7	. 125	. 223	. 259	.
8	. 123	. 240	. 254	.
9	. 124	. 247	. 250	.
10	. 117	. 248	-	.

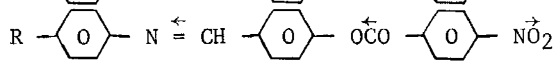
- the reentrant sequence I N S_A S_C N_{re} S_A in a mixture
- I N S_A S_C S_{C_2}.

3. FAMILY 3 : The longitudinal dipolar moments of X and Y are antiparallel with that of CN or NO_2 group. The four corresponding series are :

3A CN :


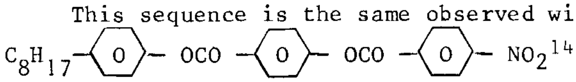
3A NO_2 :


3B CN :


3B NO_2 :


* Series 3A CN (Table IX). This is the second series after the dibenzoate[13] one to present the bilayered smectic A phase (S_{A_2}). The two first compounds (R = $C_6H_{13}O$- and $C_7H_{15}O$-) exhibit monolayered smectic A (S_{A_1}) and nematic phases. The octyloxy derivative in addition to these two phases, probably displays another antiphase $S_{\tilde{A}}$. The nonyloxy and decyloxy derivatives present the sequence :

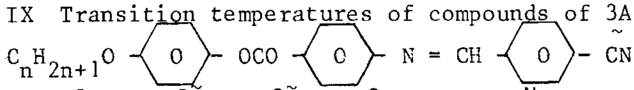
K S_{A_2} $S_{\tilde{C}}$ S_A N I

This sequence is the same observed with the compound

[14] and these phases were respectively miscible.

The derivatives of this series do not exhibit the reentrant phanomenon in pure compounds as observed in the other cyano series.

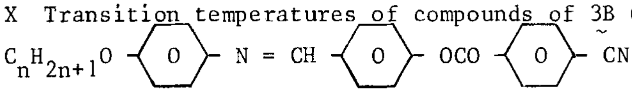
* Series 3B CN[15] (Table X). Ten derivatives were synthesized with R = C_4H_9O → $C_{12}H_{25}O$ and $C_{14}H_{29}O$. The reentrant phenomenon was also not observed in pure compounds which exhibit the novel biaxial $S_{\tilde{C}}$ and S_{C_2} phases. These two phases have been identified by the miscibility method with the same se-

TABLE IX Transition temperatures of compounds of $\underset{\sim}{3A}$ CN



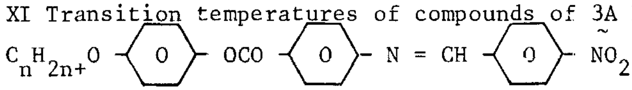
n	K	S_{A_2}	$S_{\tilde{A}}$	$S_{\tilde{C}}$	S_A	N	I
6	. 120	–	–	–	. 147.5	. 277	.
7	. 114	–	–	–	. 149	. 270	.
8	. 113	–	. 132	–	. 149	. 266	.
9	. 116	. 137	–	. 144	. 163	. 251	.
10	. 113	. 138	–	. 141	. 210	. 248	.

TABLE X Transition temperatures of compounds of $\underset{\sim}{3B}$ CN



n	K	S_{C_2}	$S_{\tilde{C}}$	S_A	N	I
4	. 128	–	–	. 179	. 296	.
5	. 122.5	–	–	. 181	. 287	.
6	. 120	–	–	. 181.5	. 279	.
7	. 114	–	(.)	. 178	. 271	.
8	. 122	–	(. 119)	. 172	. 262	.
9	. 125	–	. 154	. 212	. 257	.
10	. 124	(. 114)	. 142	. 236	. 252	.
11	. 126	(. 125	. 131	. 239	. 246	.
12	. 124	. 129	–	. 240.5	. 242	.
14	. 125	. 131	–	. 238	–	.

TABLE XI Transition temperatures of compounds of $\underset{\sim}{3A}$ NO_2



n	K	S_{C_1}	S_{A_1}	S_{A_d}	N	I
8	. 138	–	(. 128)	–	. 253	.
9	. 134	(. 129)	–	–	. 244	.
10	. 130	. 131	–	–	. 242	.
11	. 128	. 142	–	. 221	. 236	.
12	. 128	. 136	–	. 224	. 232	.

quence of $DB_{10}ONO_2$ (Fig. 7) and by X-ray analysis (for the S_{C_2}, d ≃ 56 Å and ℓ = 30 Å). We must point out that the $S_{\tilde{C}}$ phase presents a maximum stability temperature with the nonyloxy derivative.

* Series 3A NO_2 (Table XI). This is the first polar series which probably exhibits the S_{C_1} phase. Its comportement is similar to the S_{A_1} one. It presents a temperature of maximum stability with the undecyloxy derivative. An interesting fact in this series is the competition between S_{A_1} and S_{C_1} phases. The octyloxy derivative shows nematic and metastable S_{A_1} phases while the nonyloxy and decyloxy derivatives present nematic and S_{C_1} phases. From the undecyloxy derivative the partially bilayered S_{A_d} phase appears. The mixtures of two homologues ($C_{10}H_{21}O$- and $C_{11}H_{23}O$-) show the enantiotropic reentrant sequence K S_C N_{re} S_A N I and a new triple point N_{re}, S_A, S_C[2,16,17] (Fig. 8). X-ray investigations[17] were performed with the pure undecyloxy derivative. We find in the high temperature S_A phase that the layer spacing d is somewhat larger than the molecular length ℓ ($\frac{d}{\ell} \simeq 1.1 - 1.2$). This layer spacing decreases as the temperature decreases and at $S_A - S_C$ phase transition the ratio $\frac{d}{\ell}$ is close to 1 (this ratio is equal to 0.96 in the S_{C_1} phase when the temperature is 130°C). The same result was obtained with the reentrant mixtures.

* Series 3B NO_2 (Table XII). Ten compounds of this series were synthesized (n = 4 → 12, 14) and they show S_A and N phases or only S_A phase. No reentrant phenomenon or no novel phase was found.

Conclusion for the family 3. This family leads as the dibenzoate series (DB NO_2) to the new mesophases $S_{\tilde{A}}$, $S_{\tilde{C}}$ and shows the nitro end group is in this case more favourable to reen-

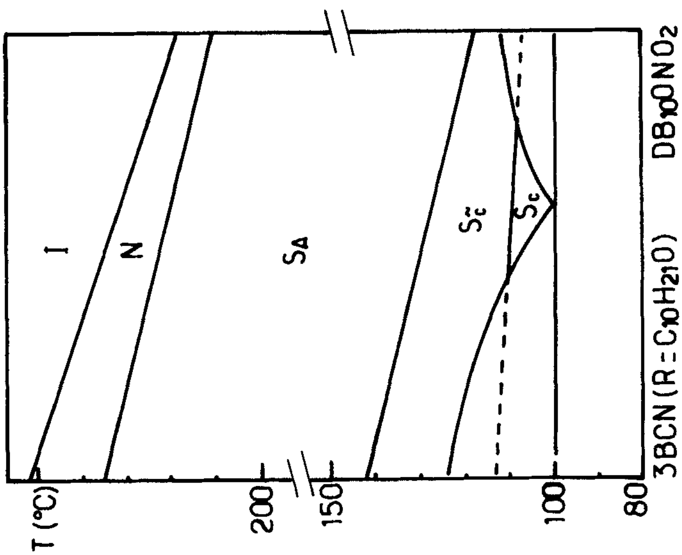


Fig. 7 : Phase diagram of mixtures

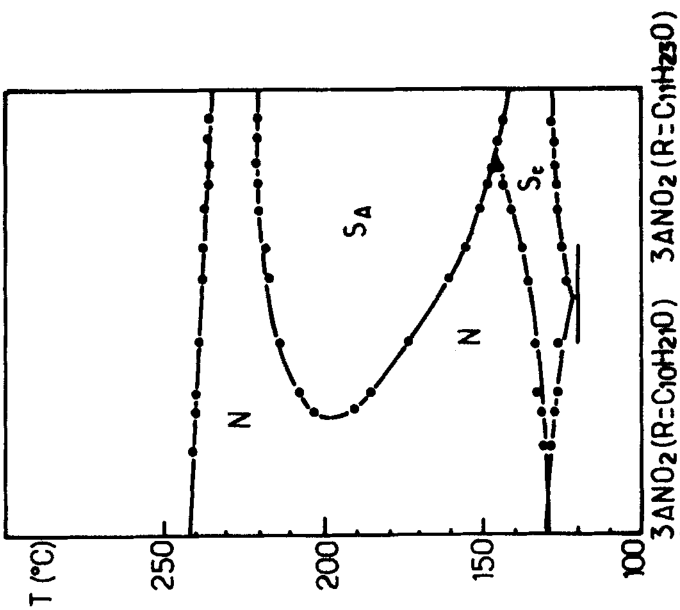
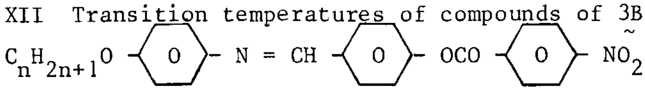


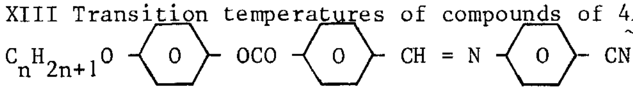
Fig. 8 : Phase diagram of mixtures

TABLE XII Transition temperatures of compounds of 3B NO_2



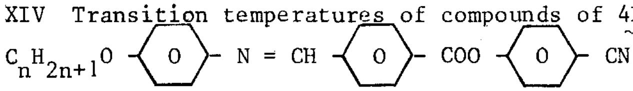
n	K		S_A		N		I
4	.	140	.	154	.	281	.
5	.	123	.	165	.	267	.
6	.	124.5	.	173	.	263	.
7	.	114	.	180	.	254	.
8	.	121	.	196	.	252	.
9	.	109	.	227	.	246	.
10	.	112	.	235	.	242	.
11	.	110	.	239	.	240	.
12	.	112	.	237	–		.
14	.	114	.	234	–		.

TABLE XIII Transition temperatures of compounds of 4A CN



n	K		S_{C_2}		$S_{\tilde{C}}$		S_C		S_A		N		I
7	.	103	–		.	105.5	–		.	171	.	262	.
8	.	102	(.	99)	.	108	.	109	.	206	.	258	.
9	.	98	.	116	–		–		.	226	.	247	.
10	.	100	.	125	–		–		.	235	.	245	.
11	.	98.5	.	127	–		–		.	242	–		.
12	.	99	.	132	–		–		.	237	–		.

TABLE XIV Transition temperatures of compounds of 4B CN

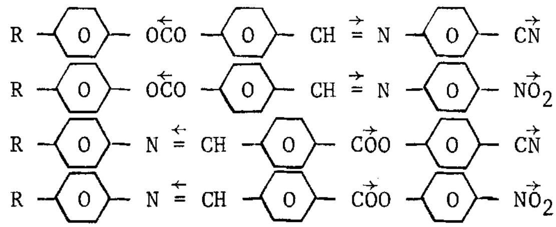


n	K		S_A		N		I
7	.	134	–		.	262	.
8	.	133	–		.	255	.
9	.	134	.	212	.	248	.
10	.	127	.	229	.	243	.

trant phenomenon than cyano end group (in the families **1** and **2**).

4. FAMILY **4**. The longitudinal dipolar moments of Y and CN or NO_2 are in the same sense while that of X is antiparallel. Four series are obtained :

4A CN :
4A NO_2 :
4B CN :
4B NO_2 :



* Series **4A** CN (Table XIII). As **3A** CN and **3B** CN, this series presents the smectic phase made of ribbons $S_{\tilde{C}}$ and the bilayered smectic C (S_{C_2}). The more interesting sequence is :

K S_{C_2} $S_{\tilde{C}}$ S_C S_A N I

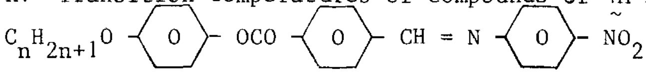
The reentrant phenomenon was not observed in pure compounds.

* Series **4B** CN (Table XIV). The two first compounds ($C_7H_{15}O$ and $C_8H_{17}O$) only show nematic phases while the nonyloxy derivative presents smectic S_A and N phases. This same behavior was observed with reentrant series. As a matter of fact the mixtures of the octyloxy and nonyloxy derivatives exhibit a reentrant nematic phase.

* Series **4A** NO_2 (Table XV) and **4B** NO_2 (Table XVI). These two series exhibit the reentrant phenomenon in pure compounds. The observed sequence is :

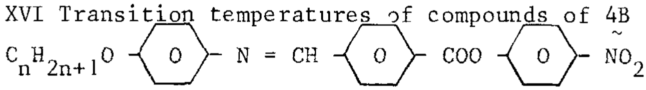
K N_{re} S_C S_A N I

TABLE XV Transition temperatures of compounds of 4A NO_2



n	K		N_{re}	S_C	S_A		N		I
7	.	101	-	-	-		.	244	.
8	.	87	(. 64)	(. 67)	.	186	.	241	.
9	.	89	-	(. 62)	.	218	.	237	.
10	.	89	-	-	.	227	.	234	.

TABLE XVI Transition temperatures of compounds of 4B NO_2



n	K		N_{re}	S_C	S_A		N		I
6	.	130	-	-	-		.	255	.
7	.	124	-	-	-		.	246	.
8	.	115	. 132	-	.	196	.	243	.
9	.	121	(. 80)	(. 82)	.	221	.	239	.
10	.	118	-	-	.	228	.	234	.

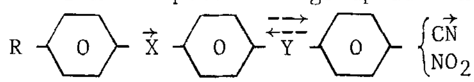
Conclusion for the family 4. As family 3, the cyano compounds present the new $S_{\tilde{C}}$ and S_{C_2} phases while the nitro compounds show reentrant nematic phases.

CONCLUSION

With different longitudinal dipolar moments of X and Y we have studied the influence of the polar end group - CN or NO_2 on the reentrant phenomenon and the appearance of the new phases $S_{\tilde{A}}$, $S_{\tilde{C}}$, we must point out some following interesting features.

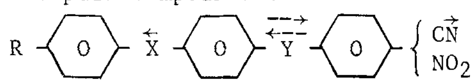
* Reentrant phenomenon

In the families 1 and 2 in which the longitudinal dipolar moments of X and polar end group are in the same sense :

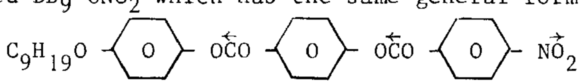


the cyano group is very more favourable to reentrant phenomenon than the nitro one.

A quite contrary result was obtained with families 3 and 4 in which the longitudinal polar moments of X and cyano and nitro are antiparallel : the reentrant phenomenon only exists in nitro pure compounds :



An exciting example was recently reported with the so-called DB_9 ONO_2 which has the same general formula type :



K 109(S_{C_2}) $S_{\tilde{C}}$ 118 S_{A_1} 124 N_{re} 127 S_{A_d} 138 N_{re} 156 S_A 195 N 224 I

The other reentrant sequences are :

K	S_A	N_{re}	S_A	N	I	
K	N_{re}	S_C	S_A	N	I	
K	S_A	N_{re}	S_C	S_A	N	I
K	S_C	N_{re}	S_A	N	I	

* Novel phases $S_{\tilde{A}}$, $S_{\tilde{C}}$

Up to now these novel phases $S_{\tilde{A}}$ and $S_{\tilde{C}}$ were only found in the families 3 (all two series) and 4 (only one series). In these families, the different smectic A and C phases are also present, for example :

S_{A_2} S_{A_1} S_{A_d}

S_{C_2} S_{C_1} S_{C_d}

* Transition $S_C - S_C$

Only one compound (in the series 2B CN) offers a directly transition $S_{C_2} - S_C$ with the sequence :

K S_{C_2} S_C S_A N I

Between the S_{C_2} and S_C phases, another tilted phase can appear with the sequence :

K S_{C_2} $S_{\tilde{C}}$ S_C S_A N I

in a pure compound of 4A CN series.

Now, we are able to foresee the three benzene ring compound architecture which displays the expected properties.

1. To obtain the reentrant phenomenon
   - with cyano end group, the longitudinal dipolar moment of X must be in the same sense.
   - with nitro end group, the longitudinal dipolar moment of X must be in opposite sense.
2. To obtain new phases $S_{\tilde{A}}$ and $S_{\tilde{C}}$, with both cyano and nitro end groups, the longitudinal dipolar moment of X must be in opposite sense.

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