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PHASE DIAGRAMS OF NEW COMPOUNDS WITH NEMATIC REENTRANT MESOPHASES

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Abstract

Two new series of compounds exhibiting nematic and smectic reentrant mesophases are presented here ; the first one is 4-n-alkoxy benzoyloxybenzylidene 4'-cyanoaniline series, the second one, the 1-(4-n-alkylbenzoyloxyphenyl) 2-(4'-cyanophenyl) ethane series. Isobaric binary phase diagrams are plotted for each compound by means of the contact method and the mesophases so identified.

Introduction

Isobaric phase diagrams of binary mixtures[1,2,3,4,5] and thermobarograms of some pure compounds[6,7,8] or mixtures[8] show that in some mesogens the succession of the mesophases is nematic (N), smectic A (S_A) and N. Isobaric phase diagrams of binary mixtures[9,10,11,12] and R-X studies[4,13] let appear the existence of a lower temperature S_A phase, so the succession of the mesophases is S_A, N, S_A, N.

We present here two new series in which long-chain compounds exhibit the nematic reentrant phenomenon.

Identification of the reentrant stable or virtual mesophases

The two series of compounds studied here, have the general following formula :

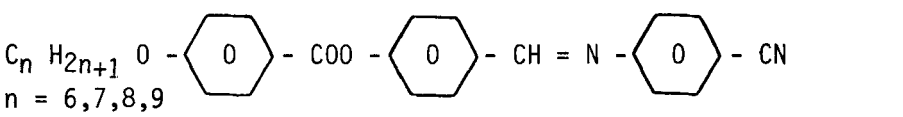
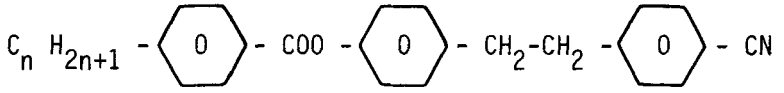


Table I : Temperatures and enthalpies of transition of : R-⟨0⟩-COO-⟨0⟩-X-⟨0⟩-CN

nr	X	R	K'	K	T_m	S_A	T"	N	T'	S_A	T	N	T_i	I	
1	CH=CH	n.$C_8H_{17}O$	60	-	95.5 *7.0*	-	[94.1] *0.026*	-	137.8 *0.011*	-	248.5 *0.017*	-	282.5	-	a)
			[78] *4.0*	-											
2	CH=N	n.$C_6H_{13}O$		-	113.5 *7.7*	-		-		-	[91] b)	-	274.5	-	
3		n.$C_7H_{15}O$		-	114.5 *7.3*	-		-		-	[70] b)	-	263.5	-	
			[108]	-		-		-		-					
4		n.$C_8H_{17}O$		-	107.5 *8.67*	-		-	153 b)	-	197.5 b)	-	255 *0.29*	-	
5		n.$C_9H_{19}O$		-	96 *9.8*	-	[40] b)	-	[92] b)	-	228 b)	-	251 *0.25*	-	
6	CH_2-CH_2	n.C_7H_{15}		-	89 *7.3*	-		-		-		-	150 *0.54*	-	
7		n.C_8H_{17}		-	92 *9.9*	-		-	[72] b)	-	96 b)	-	144 *0.92*	-	

a) data from references 11 and 12, except for the melting enthalpies and the K-K' and K'-S_A transition temperatures.

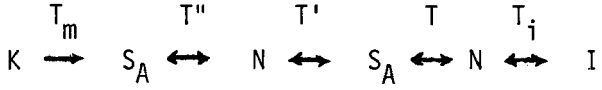
b) temperatures only determined by microscopic observation (transition enthalpies too weak or transitions unobservable on the pure compound).



n = 7,8

The mesophases of these compounds, listed in Table I, were examined by differential scanning calorimetry (DSC 1B Perkin Elmer) and by observation with a polarizing microscope equipped with a programmable heating stage (Mettler FP 5).

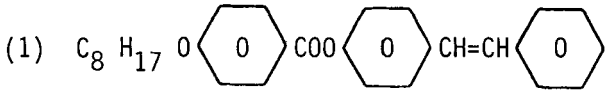
The notations of the transitions are as following :

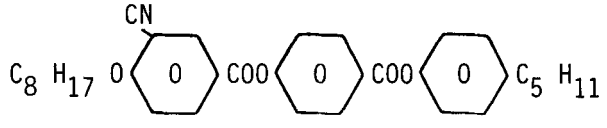


with T_m melting temperature, and T_i temperature of clarification. The microscopic observation of the S_A-N transitions of the studied compounds is often uneasy because the two textures are perfectly homeotropic. To visualize these transitions, the preparation is done on a roughed glass which, by means of the irregularities, induces defects in the texture, especially in the nematic phase. The insertion of a wave retardation plate, with its neutral lines at 45° from the principal sections of the polarizers, get the observation more easy. Very often the transition at the temperature T" is virtual and cannot be observed on supercooled droplets[14]. These transitions are thus determined by the method of the binary isobaric phase diagrams[15]. The mesophases were identified by means of the miscibility rules of the mesogens[16].

Miscibility results

- The following compound :

(1)  was first identified as S_C, S_A, N[17]. The "S_C" phase is in fact a N reentrant phase[9,10,12,13]. Then true binary diagram of the compound nr 1 with :



(see ref. 17) is plotted here (figure 1). The temperatures of transition and the enthalpies of compound nr 1 are

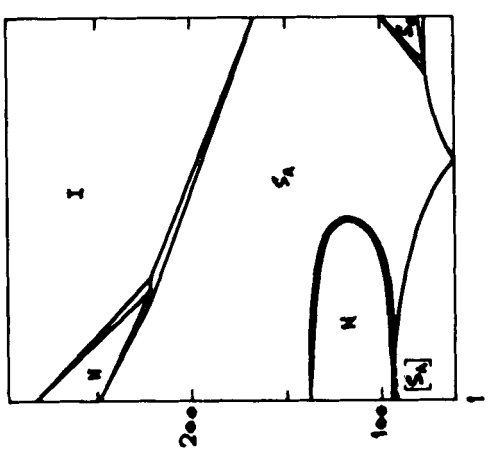


Fig. 1 : Isobaric phase diagram of the compound nr 1 and the 3-cyano-4-n-octyloxybenzoyloxy 4'-n-pentylbenzoate17.

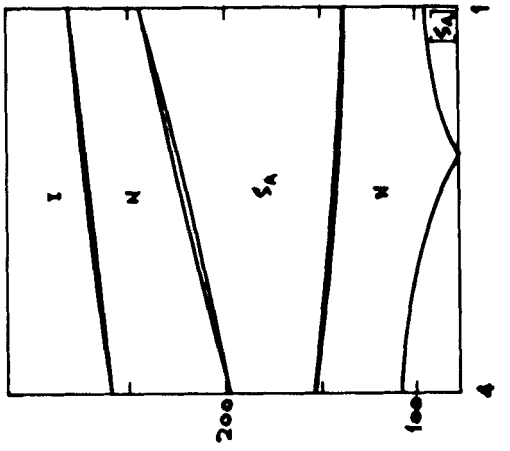


Fig. 2 : Isobaric phase diagram of the compound nr 4 and the compound nr 1.

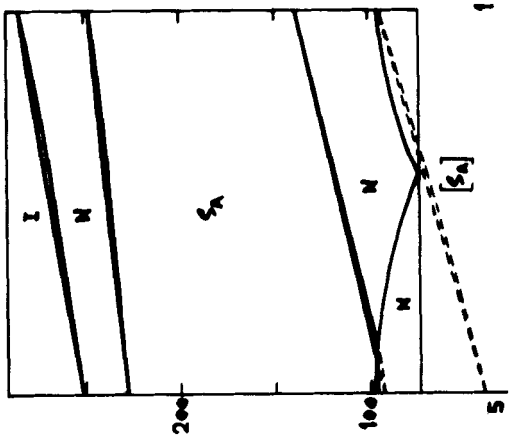


Fig. 3 : Isobaric phase diagram of the compound nr 5 and the compound nr 1.

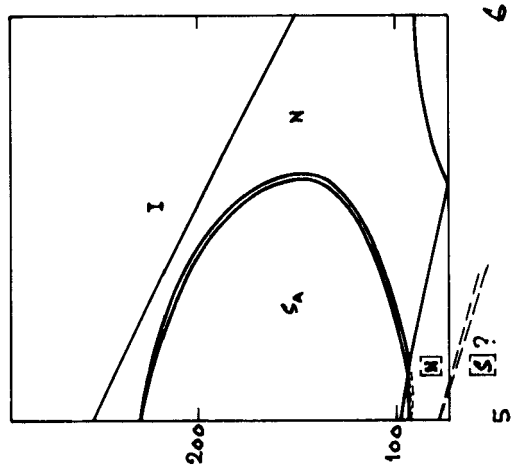


Fig. 4 : Isobaric phase diagram of the compound nr 5 and the compound nr 7.

Fig. 5 : Isobaric phase diagram of the compound nr 5 and the compound nr 6.

listed in Table I. This compound exhibits successively the monotropic smectic A phase and enantiotropic nematic reentrant phases : "napolitean ice-cream type"12.

- The mesophases of the compound nr 4 are identified by isomorphy with the previous compound (fig. 2) ; the eutectic mixture of these two compounds melts at 77°C, no S_A-N transition (T") occurs when cooling the mixture from the nematic phase, before the recrystallization at 50°C. The T" transition could not be determined anymore by the method of the supercooled droplets.

- The mesophases of the compound nr 5 are identified with the compound nr 1 too (figure 3). The S_A-N transition (T') may be observed on supercooling at T' = 92°C. But the N-S_A transition (T") cannot be observed directly ; a large mosaïc-textured mesophase appears by cooling and gives, by heating, the reentrant nematic phase at 79°C. So the transition T" can only be obtained by extrapolation from the S_A-N spindle in the binary phase diagram (figure 3) : T" = 40°C.

- The compounds nr 2 and nr 3 exhibit only a stable nematic mesophase. The microscopic observation of supercooled small drops of these compounds let us determine a metastable S_A-N transition : for the compound nr 2 T = 91°C and for the compound nr 3 T = 70°C. The N phase of nr 2 is isomorphic with the two nematic phases of nr 1 ; a stable low temperature S_A phase appears in their binary diagram over the eutectic point (quite rectilinear spindle[14]). The N phase of nr 3 is isomorphic with the two nematic phases of nr 4. In these two diagrams, a smectic A area is separated by a spindle admitting a tangent parallel to the temperature axis[18].

- The mesophases of the compound nr 7[19] are identified from these of the compound nr 5 (figure 4). Supercooled droplets of the former crystallize always before the T' transistion so this temperature is deducted from the binary phase diagram of the figure 4 : T' = 72°C.

- The mesophase of the compound nr 6 is identified by isomorphy with that of the compound nr 5 (figure 5). This diagram confirms the existence of the nematic reentrant mesophase of the compound nr 5 and shows that for the compound nr 6 the T temperature is lower than 40°C.

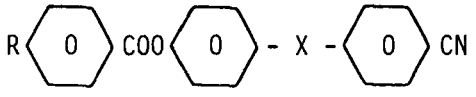
All the obtained results are listed in the table I.

Discussion

The two series of compounds presented here exhibit the

N reentrant phenomenon. In the 4-n-alkoxybenzoyloxybenzylidene-4'-cyanoaniline series, the 4-n-octyloxy compound is N reentrant stable, the 4-n-nonyloxy, N reentrant metastable. In the later compound a S_A virtual mesophase exists at temperature lower than the N reentrant mesophase. In the 1-(4-n-alkylbenzoyloxyphenyl) 2-(4'-cyanophenyl) ethane series, the n-octyl is N reentrant virtual.

So actually the N reentrant phenomenon appears systematically in the series with the following general formula :



with R = n-alkyl or n-alkoxy and X beeing a single bond[8] an ethylenic[12], acetylenic[10,21], azo[20], azomethine or ethane bond.

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