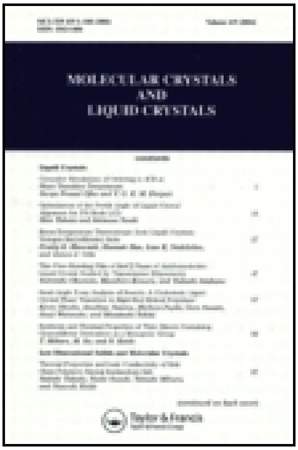

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Mesogenic properties of liquid crystals having a chiral semiflexible joint

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Mesogenic properties of liquid crystals having a chiral semiflexible joint

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Two homologous series of mesogenic enantiomers with chiral semiflexible joint, -C*H(CH_3)CH_2COO-, are examined. High twist power and presence of blue phases with short lattice period are found for eleven examined compounds. Some effects of chirality in reentrant system are discussed. On phase diagram of enantiomers the SmA_d phase area is shifted toward longer homologues as compared to racemates. In result, an island of the SmA_d phase in the cholesteric sea exists on binary phase diagrams of R- and S- enantiomers. Triple divergence of the pitch in the cholesteric phase of a pure compound is observed.

1. INTRODUCTION

Almost since the discovery of cholesterics, chirality was one of the most important topics in liquid crystal research.[1] A great effort has been devoted to understand relations between structure of chiral molecules and their mesogenic properties. It is known that some properties of mesophases with helical structure can be directly related to molecular structures.[2-4] It, generally, has been found, that when steric hindrances to the rotation of a molecular asymmetry center increase, phases with short helical pitch are formed. It is also well known, that chirality might generate new helical mesophases, for example blue phases[5], recently discovered twist-grain phases[6] and ferri- or antiferroelectric ones.[7]

Chirality is also a factor influencing mesomorphic phase transitions.[8-10] It seems that the particularly sensitive to this factor are transitions which are second or very weak first order, since in such transitions a part of free energy associated to the helical twist might play an important role.[11] For this reason systems with reentrant phases[12] seem adequate to study chiral effects. On a typical phase diagram of reentrant liquid crystals there are areas of two smectic phases, partly bilayer SmA_d and monolayer SmA_1 ones, separated by the nematic phase, N_{re}. Close to the appex of the SmA_d area, phase transitions become second order and hence might be significantly influenced by strong chirality.

Chirality is introduced into typical mesogenic molecules by placing an asymmetry center in a flexible terminal chain. Recently, mesogens with rigid chiral rings are synthesized and studied, as well.[13] Mesogens with chiral center incorporated into flexible molecular joints are also known.[14] However, no resulting molecules assure both: high twist power and existence of chiral reentrant phases.[15] Therefore we had to propose some new molecular reentrant structures. In this work we describe mesophase properties of compounds with a novel semiflexible moiety, $-C_6H_4-CH(CH_3)CH_2COO-$[16], in its optically active variant. From two series:
mHAZO: $H-C_6H_4-C^*H(CH_3)CH_2COO-C_6H_4-N = N-C_6H_4-OC_mH_{2m+1}$
mNAZY: $O_2N-C_6H_4-C^*H(CH_3)CH_2COO-C_6H_4-N(O)N-C_6H_4-OC_mH_{2m+1}$
the former was examined to study twist power, the latter - reentrant phenomena in chiral systems. Properties of some structurally related compounds of the series:
mHAZY: $H-C_6H_4-C^*H(CH_3)CH_2COO-C_6H_4-N(O)N-C_6H_4-OC_mH_{2m+1}$
are also reported for comparison.

2. EXPERIMENTAL

Compounds were synthesized according to the reaction scheme 1. Their phase transitions were detected by optical observations (Zeiss Jenapol-U microscope and Mettler HT82 hot stage) and differential scanning calorimetry (Perkin-Elmer DSC-7). DSC runs were routinely taken at 5°C/min scan. Runs requiring resolution of overlapped phase transition peaks were taken at lower scans. Heating at rates 0.5 to 0.2°C/min was optimal to detect phase transitions involving blue phases and determine their temperatures.

3. RESULTS AND DISCUSSION

3.1. Mesogenic properties of (-)-HAZO compounds

Phase transition enthalpies and temperatures for mHAZO series are collected in Tab.I. When studied microscopically, the compounds appear to be enantiotropic nematics. However, DSC measurements reveal existence of phases intermediate between isotropic and cholesteric phases. From phase sequence and their temperature range it is obvious that these are blue phases. On thermograms for homologues m = 2, 3, 4, 6 four peaks corresponding to N*-BPI, BPI-BPII, BPII-BPIII, and BPIII-Iso phase transitions were observed (Fig. 2). Homologues m = 1 and 12 were found to exhibit only three peaks, which indicate that for these two substances one of the blue phase is missing, probably because of lower twist. The temperature range of blue phases in (-)-mHAZO compounds is shown in Fig. 3.

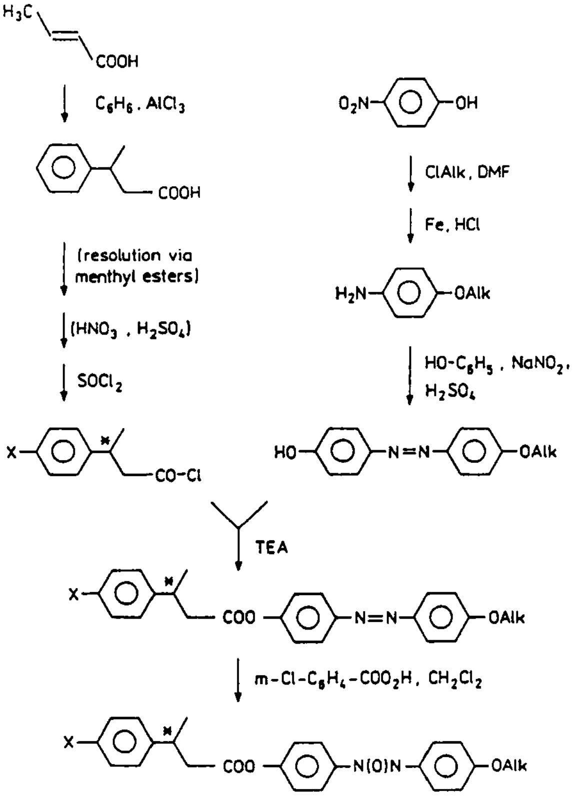

FIGURE 1 Synthetic scheme for examined series. X = H, O_2N.

The occurrence of the blue phases suggests rather high ability of the novel chiral center to induce helical ordering. However, direct determination of helical pitch for pure HAZO compounds from transmission or reflection spectra was impossible for strong light absorption and photosensitivity of the azo group. The Cano method was applicable only for compounds to be examined when diluted by standard nematics. We checked, for (-)-HAZO in PCB, that inverse of the pitch,

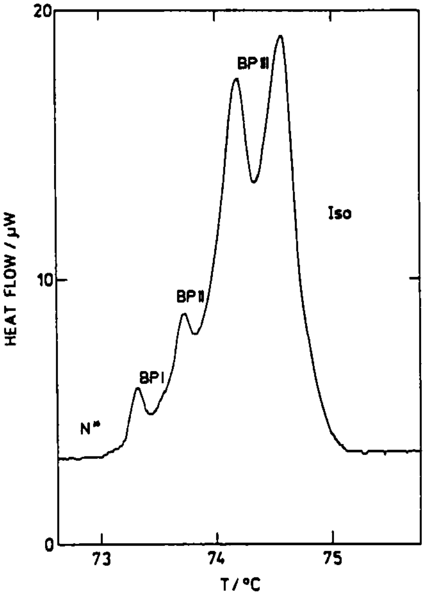

FIGURE 2 DSC scan (0.2°C/min., 1 mg sample) through the blue phases in (-)-6HAZO.

p^{-1}, was linear with chiral substance concentration (see Fig.4a). This linearity allows studies of the twist power, $\beta = 1/(pc)$, in the homologue series for constant concentration of chiral dopant (0.25 mole fraction). Results are presented in Fig.4b. Of interest are non-monotonous dependence on the terminal chain length as well as pronounced even-odd effect.

For higher dopant concentrations (above 0.5 mole fraction) Grandjean - Cano steps in the blue phase[17] were detected. Extrapolation of the data presented in Fig.4a indicates that in pure (-)-1HAZO helical pitch is of the order of 0.2 μm, thus lattice period of blue phase is of the order of 0.3 μm. For lattice of this size, Bragg-like reflections occur in the UV region, what explains why blue phases are not detected by visual observation.

Described herein azo-compounds are of limited applicability, with regard to their photosensitivity and relatively high melting temperatures. More promising derivatives can be easily synthesized by simple molecular modifications, e.g. by exchanging the azo to azoxy group. For example, no liquid crystalline phases were observed for (-)-17HAZO due to its high melting point (see Tab.I). In comparison, (-)-17HAZY compound, having the azoxy group, is an enantiotropic cholesteric and exhibits also monotropic SmA and SmC* phases.

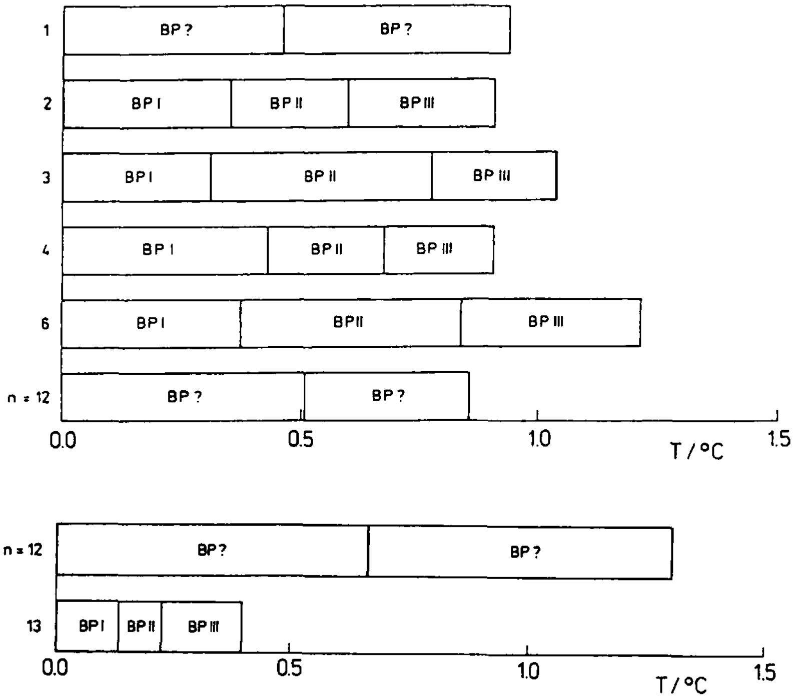

FIGURE 3 Temperature range of blue phases in (-)-mHAZO (upper part) and (-)-mNAZY compounds. In (-)-1HAZO, (-)-12HAZO and (-)-12NAZY one of the phases is missing.

TABLE I Optical activity, $[\alpha]^{20}_{589}$ (CHCl$_3$) c = 1, temperatures (in °C) and, in parentheses, enthalpies (in J/g) of phase transitions for compounds (-)-mHAZO and (-)-mHAZY.

m	$[\alpha]^{20}_{589}$	Cry		N*		BP[a]		Iso
HAZO series:								
1	-81.2		85.0 (96.4)		53.05		54.0 (0.9)	
2	-74.7		91.0 (86.2)		54.0		85.0 (1.4)	
3	-78.1		90.8 (110.3)		62.45[b]		63.5 (1.6)[b]	
4	-79.1		69.5 (80.9)		77.55		78.5 (2.0)	
6	-72.6		76.9 (92.0)		73.75		75.0 (1.5)	
12	-61.2		81.7 (~44)		71.6		72.5 (2.3)	
17	-54.0		84.8 (102.3)		-		-	
HAZY series:								
17	-64.6		76.4 (90.8)[c]		80.7		82.0 (3.0)	

[a] Total enthalpy for unresolved peaks including the clearing and the transitions between blue phases.

[b] Temperatures lower than expected for pure compound.

[c] Also monotropic phases sequence: SmC* 70.6 (0.07) SmA 73.6 (1.9) N*.

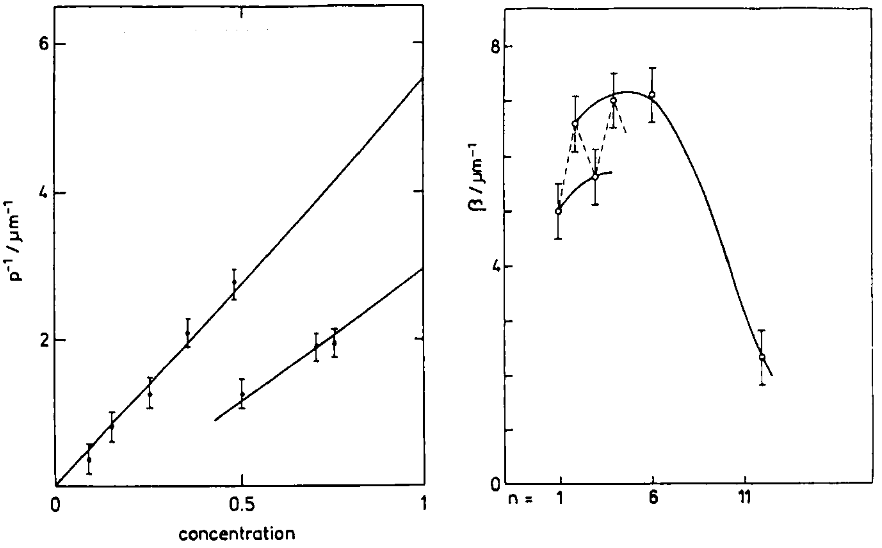

FIGURE 4 (a) - left: inverse pitch, p^{-1}, as a function of concentration of chiral (-)-1HAZO in PCB. For concentrations $c \geq 0.5$ (in mole fraction) points are related to the distance of Cano lines in blue phase. (b) - right: helical twist power, $\beta = 1/(pc)$, in compounds (-)-mHAZO. Helical pitch was determined for 0.25 mole fraction of chiral dopant in PCB. In all cases the helix is right handed.

3.2. Mesogenic properties of (-)-mNAZY compounds

Phase and thermodynamic properties of racemic compounds were extensively discussed previously.[16] In that series reentrant nematic was observed for homologues with $m \geq 12$. The apex of SmA area on binary phase diagram was located at $m_0 = 11.89$. In this work we observe that properties of enantiomeric 12NAZY and 13NAZY compounds are different. On the contrary to racemate, we did not detect SmA_d and N_{re} phases for the former compound. For the latter one, temperature range of SmA_d phase is distinctly narrower than in racemate (see Tab.II).

Different phase behavior of enantiomers and racemates was confirmed by studies of some binary phase diagrams. The diagrams for the system of enantiomers, (-)-12NAZY and (-)-13NAZY are shown in Fig.5a. It is seen, that the appex of SmA_d phase area is located at $m_0 = 12.83$. Thus it is significantly shifted toward longer homologues as compared to the racemates. Furthermore, studies of system (-)-12NAZY - (+/-)-12NAZY were carried out. Our results clearly show that for the mixtures of both 12NAZY enantiomers, an unusual topology of phase diagram with an island of the SmA_d phase on the cholesteric sea has to be obtained (Fig.5b). Studies of the phase surface determined in the three-dimensional space (temperature, chain length, chirality) suggest that the smectic island results from the presence of chiral discrimination effect.[18]

TABLE II Temperatures (in °C) and, in parenthesis, enthalpies (in J/g) of phase transitions for racemic and enantiomeric mNAZY compounds.

m	Cry	SmA_1	N_{re}	SmA_d	N	BP	Iso
racemates:							
12		73.5	92.0(0.01)	102.0(0.00)	112.5(0.00)	121.9(3.3)	-
13		71.6	82.0(0.12)	86.1(0.15)	121.7(0.20)	122.1(4.3)	-
enantiomers:							
12		76.8(73.0)	79.0(0.04)	-	-	119.6	120.9(3.3)
13		71.2(70.1)	72.8(0.04)	95.0(0.00)	115.5(0.05)	120.1	120.5(3.6)

In order to study blue phases in reentrant systems, careful DSC measurements of enantiomeric mNAZY compounds were performed. For 12NAZY total temperature range of blue phase, ca. 1.4 °C, is comparable to that in the HAZY series. However, for 13NAZY blue phase width drastically narrows to 0.4 °C. This behaviour can be related to the different range of nematic phase in both homologes. For the longer ones, the nematic phase is narrowed, thus enhanced smectic fluctuations can be expected and, in result, formation of blue phases - suppressed.

Our DSC results for (-)-13NAZY show that there is no enthalpy changes at all or they are extremely small for three subsequent transitions between phases SmA_1-N^*_{re}-SmA_d-N^*. Continuous phase transitions require the helical pitch to diverge at each of the boundaries between twisted nematic and untwisted smectic phases[18]. In consequence, nonmonotonical temperature behavior of helical pitch is expected in the N^*_{re} phase. Such behavior was indeed observed for (-)-13NAZY. On cooling (or heating), homogenically oriented sample of this compounds reflects light in three temperature ranges. Irridiscent colours pass through blue to red (in reflection spectra) in N^* phase and from red to blue and again from blue to red, in the reentrant N^*_{re} phase, when temperature is lowered (Tab.III).

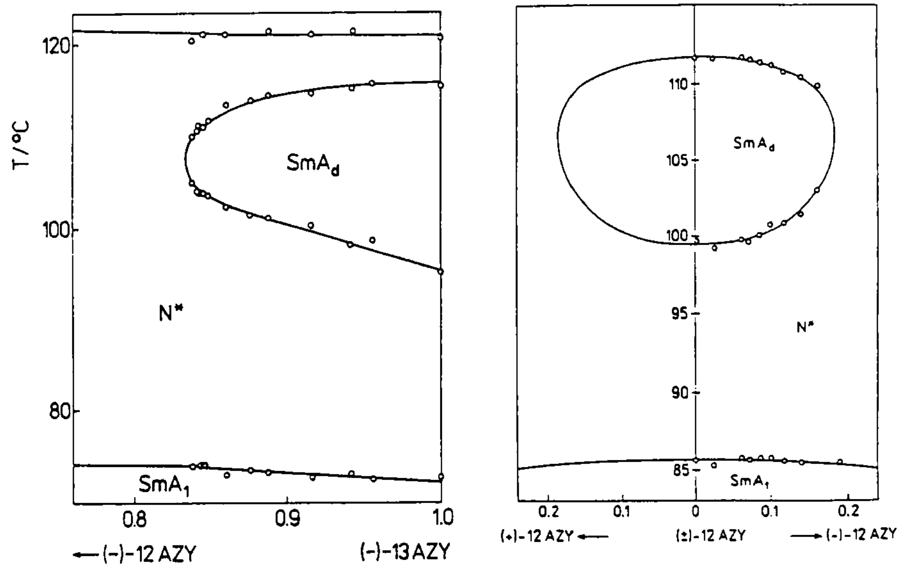

FIGURE 5 (a) - left: phase diagram for binary system (-)-12NAZY-(-)-13NAZY; Concentration expressed in mole fraction of (-)-13NAZY; (b) right: phase diagram for binary system (+)-12AZY-(-)-12AZY. Transition lines for (+/-)-12AZY-(-)-12AZY system has been reflected, in order to produce complete phase diagram for opposite isomers.

TABLE III Colours of selective light reflection from cholesteric phases of (-)-13NAZY near phase transitions to smectic phases.

T(°C)	colour	phase
116.9	blue	N*
116.2	green-yellow	near
116.0	red	SmA$_d$
93.5	red-orange	N*$_{re}$
92.6	yellow-green	near
91.5	blue	SmA$_d$
73.6	blue	N*$_{re}$
73.2	green	near
72.6	red	SmA$_1$

4. CONCLUSIONS

In conclusions, it has been found that $-C_6H_4-C^*H(CH_3)CH_2COO-$ fragment incorporated into mesogenic molecules causes large twist power of mesophases. This is attributed to the specific molecular structure in which chiral center is associated to the bulky phenyl ring. In result, blue phases with short lattice period (and no selective reflection of visible light) appear in this class of materials. In reentrant systems chirality additionally influences stability of the SmA_d phase. For enantiomers, the appex of SmA_d area is markedly shifted toward longer homologues, as comparing to racemates. In result, an island of the SmA_d phase in the cholesteric sea appears on phase diagram of (+)- and (-)-12NAZY. The vicinity of smectic phase influences blue phases stability, by disturbing their formation. Nonmonotonical, triple-divergence behaviour of helical pitch in the N* and N^*_{re} phases was found in (-)-13NAZY. This is in agreement with DSC results, which indicate near-continuous transitions through SmA_1 - N^*_{re} - SmA_d phases in this compound.

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