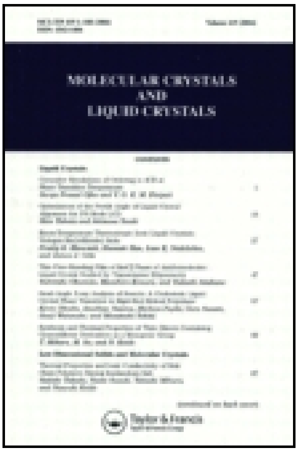

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# Effects of Polar Interactions and Molecular Packing upon the Induced Smectic Mesomorphism

L. N. Lisetski [a] , L. A. Batrachenko [a] & V. D. Panikarskaya [a]
[a] Institute for Single Crystals, Kharkov, USSR

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# EFFECTS OF POLAR INTERACTIONS AND MOLECULAR PACKING UPON THE INDUCED SMECTIC MESOMORPHISM.

L. N. LISETSKI, L. A. BATRACHENKO, V. D. PANIKARSKAYA
Institute for Single Crystals, Kharkov, USSR

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Abstract To look into the nature of intermolecular forces responsible for the induced smectic mesophase formation, model binary systems were studied comprising components of different chemical classes. Three distinct types of systems could be singled out, with translational order enhancement presumably due to (a) steric factors, (b) dipole - dipole interactions, and (c) change-transfer complex formation.

*Keywords: induced smectics, nematic mixtures, steric factors, dipole forces, complex formation, phase diagrams*

## INTRODUCTION

Formation of induced smectic mesophases in mixtures of nematics[1-3] is, perhaps, the most striking evidence of the role which can be played by specific intermolecular interactions in multicomponent liquid crystalline systems. In spite of continued attention attracted by this phenomenon[4-6], there is no universally accepted mechanism explaining such a tendency towards enhancement of the translational ordering.

Less familiar, but just as important for our understanding of liquid crystal structure on the molecular level are nematic-cholesteric mixtures, i.e., cholesterol derivatives mixed with typical nematogens. These systems are characterized by induction of extra helical twisting[7], which is presumably due to some peculiar features of interaction between molecules of different components[8]

In this paper we report our studies of the induced smectic phase formation in several types of liquid crystalline systems: (a) 4-alkyl(alkoxy)cyanobiphenyls mixed with carboxylic acids (mesogenic and non-mesogenic), (b) nematic-cholesteric mixtures, (c) 4-alkyl(alkoxy)cyanobiphenyls mixed with amino substituted compounds with anisotropic (quasimesogenic) molecules.

## EXPERIMENTAL

Phase diagrams were obtained by means of differential scanning calorimetry (Mettler TA 3000) and checked by polarization microscopy. Spectral studies were carried out using Specord M80 and Hitachi 330 spectrophotometers, the latter used also for measurements of selective transmission spectra in the cholesteric phase.

## RESULTS AND DISCUSSION

### Cyanobiphenyl-carboxylic acid systems

Formation of the induced smectic phases in the cyanobiphenyl-alkoxybenzoic acid system has been known long since[9]. Enhancement of the translational order in similar systems with cyclohexane rings substituted for the benzene ones[10] excluded apparently natural explanations based on the eventual complex formation involving $\pi$-electron systems. Stabilization of the condensed phase in the mixed Langmuir monolayers of 4-alkyl-4'-cyanoterphenyl and arahidic acid[11] did also suggest a possibility of packing features contributing to the translational ordering.

Typical results are summarized in Fig. 1. The data for non-smectogenic 7OCB were similar, taking into account its virtual $T_c$ value. In all cases increase in $T_c$ was accompanied by a marked increase in the corresponding heat of transition $\Delta H_c$. It should be noted that non-mesogenic long-chain aliphatic acids cause positive $T_c$ shifts, while 4-substituted benzoic acids not containing alkyl chains decreased thermal stability of the smectic-A phase. No spectral evidence of any specific interactions could be found.

A tentative explanation is based upon the assumption that formation of cyanobiphenyl dimers is suppressed in the mixed system due to steric influence of the much more stable carboxylic acid dimers. The general packing pattern emerging in the mixed systems, with the cyanobiphenyl molecules filling in the layers formed by the acid dimers, appears to be favourable to the translational ordering. Thus, cyanobiphenyl-carboxylic acid systems represent another class of induced smectics where, like in the so-called filled smectics[8], enhancement of translational order is caused by steric factors.

Nematic-cholesteric mixtures.

Typical phase diagrams are shown in Fig. 2. The following features should be noted:

-In all the cases smectic-C phase is quickly depressed. Close to the triple point $N^*$-A-$C^*$, S-N and N-I transition heats are (as it could be expected[12]) noticeably lower. This can be related to a decrease in the orientational order because of disorientation of tilt directions.

-While in the system cholesteryl chloride - phenyl benzoate smectic A phase is induced, smectic B phase is formed in the system cholesteryl chloride - 6OBT. (One should note that 6OBT does form monotropic smectic B phase as an individual substance). This is reflected in the fact that in this case there is no helix unwinding due to the pre-transitional phenomena (Fig.3).

-If cholesteryl chloride is replaced by cholesteryl iodide, similar phase diagrams are obtained, with even stronger tendencies towards stabilization of smectic A and B phases, which may be attributed to higher dipole moment of cholesteryl iodide (2.26 instead of 2.15).

From the data obtained, the following mechanism of the smectic phase induction is proposed:

CM-azobenzene: interaction of the lateral dipoles of the C=O and azoxy- groups naturally leads to higher translational order. The same effect, though less pronounced, can be seen in the CM-phenylbenzoate systems. On the contrary, interaction of longitudinal and lateral dipoles hinders translational (and, to smaller extent, orientational) ordering in the CM-benzylidene aniline systems. Strong interaction between antiparallel longitudinal dipoles stabilized the highly ordered smectic-B phase in the case of CC-benzylidene aniline.

Two factors are competing in CC-azobenzene and CC--phenylbenzoate systems. Upon adding of cholesteryl chloride $S_C$ phase is depressed, and effective length of the nematic molecule is increased (which is reflected in larger distances between smectic layers in the induced phase)[13] On further adding of cholesteryl chloride smectic phase is destroyed due to interaction of longitudinal and lateral dipoles. In a similar way NOBA molecules, introduced into the cholesteryl myristate matrix, assume the effective shape conforming to higher anisometry in comparison with the smectic C phase. One may say that the increase in thermal stability of the smectic A phase is due to the influence of the "virtual" smectic-A phase of the acid. When concentration of the acid is increased, its molecules (more exactly, its dimers) assume their 'natural'effective form,leading to destruction of the smectic-A and subsequent emergence of the smectic-C mesophase. A similar mechanism has been proposed for $S_{Ad}$ and $S_{A1}$ mixtures[14]. With regard to these particular systems, one should note the possibility of formation not just of the induced $S_A$ phase, but also of 'helical smectic A' and other low-temperature smectics.[15]

Cyanobiphenyl-amino substituted quasimesogene

This type of induced smectic - forming systems is relatively well known[16]; still systematic data on amino substituted compounds with anisotropic molecules would be of a certain interest. Typical results are shown in Fig. 4 ,5 and can be summarized as follows:

-For all the substances studied (except 4-aminobenzoic acid) $dT_c/dc > dT_i/dc$, i.e.,translational order is more stable with respect to this class of dopants compared with translational order.

-For some of the non-mesogenic substances $dT_c/dc>0$, i.e., in fact, induction of smectic phase does take place.

-In all the systems studied $\Delta H_c$ increased on the introduction of the dopants.

-In some cases (4,4'-aminodiphenyl, 4-aminobenzoic acid, 4-aminobiphenyl) thermal stability of the solid phase is increased, which is not correlated to the smectic phase induction. This suggests that one- and three-dimensional translational ordering may be governed by different mechanisms.

IR spectroscopy data are consistent with strong variation of the valence angle $\begin{matrix}H\\H\end{matrix}\rangle N$ due to the non-symmetrical hydrogen bond formation in the mixed systems,

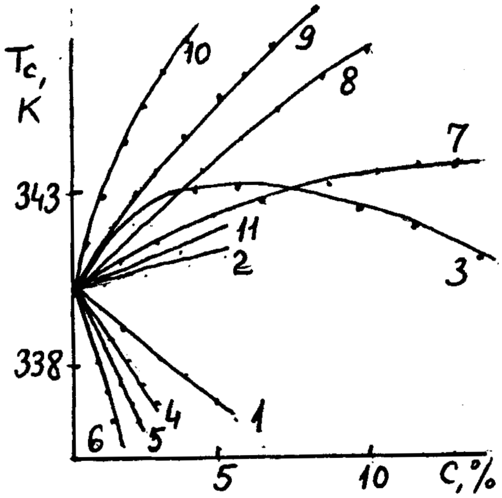


FIGURE 1. Carboxylic acid dopants affecting SA -N transition temperature of 8OCB: 1-caproic, 2-undecanoic, 3-stearic, 4-benzoic, 5- 4-nitrobenzoic, 6- 4-aminobenzoic, 7- 4-butulbenzoic, 8- 4-hexylcychexanecarboxylic, 9- 4-butylbenzoic, 10- 4-nonylbenzoic, 11- 4-octyl-4'-biphenylcarboxylic.

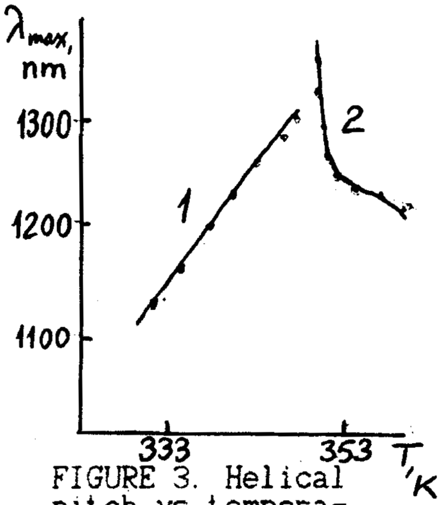


FIGURE 3. Helical pitch vs. temperature for 34.7% CM-6OBT (curve 1) and 24.0% CC + 6OP8OB (curve 2).

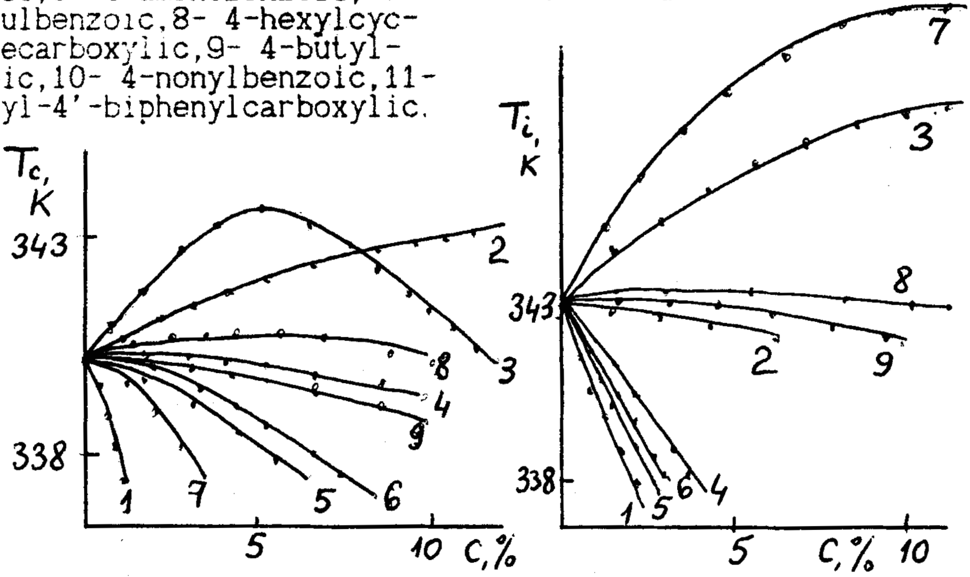


FIGURE 4,5. Amino substituted dopants affecting nemating-isotropic and smectic-A - nematic transition temperatures of 8OCB: 1 - 2-aminobiphenyl; 2 - 4-aminobiphenyl, 3 - 4,4'-diaminobiphenyl; 4 - 4-metoxyaniline 5 - 4-metylaniline; 6 - 4-butylaniline; 7 - 4-aminobenzoic acid; 8 - 3-aminopropionic acid; 9 - I-arginine.

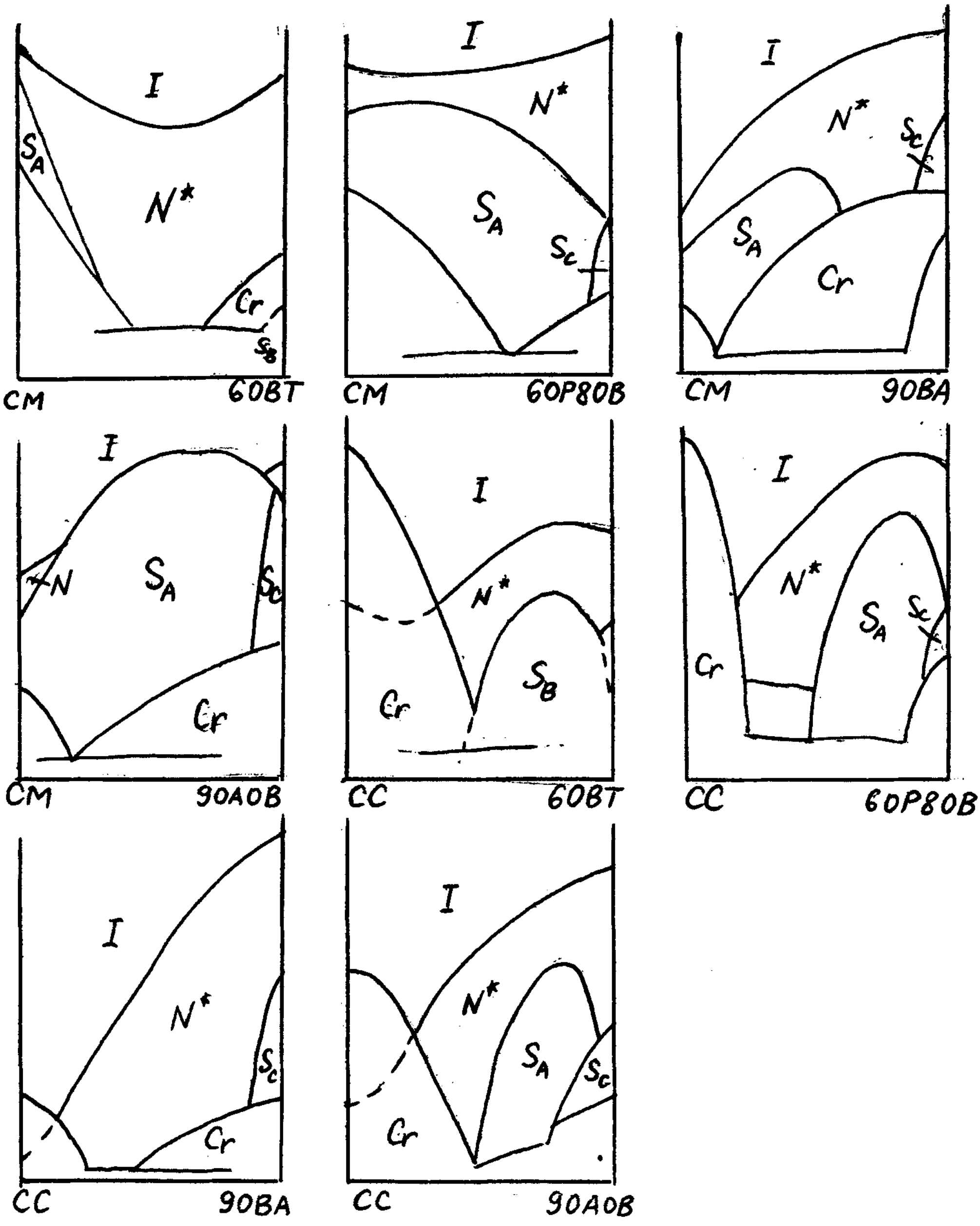
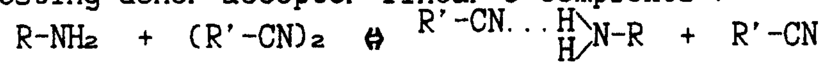


FIGURE 2. Phase diagrams of nematic-cholesteric mixtures. CM - cholesteryl myristate; CC - cholesteryl chloride; 6OBT - 4-hexyloxybenzylidene-4'-toluidine; 6OP8OB - 4-hexyloxyphenyl-4'-octyloxybenzoate; 9OBA - 4-nonyloxybenzoic acid; 9OAOB - 4,4'-dinonyloxyazoxybenzene.

suggesting donor-acceptor linear $\sigma$-complexes :



$$R\text{-}NH_2 \;+\; (R'\text{-}CN)_2 \;\Leftrightarrow\; R'\text{-}CN\cdots{}^{H}_{H}\!\!>\!N\text{-}R \;+\; R'\text{-}CN$$

When the complex formed is longer than the cyanobiphenyl dimers, $dT_i/dc>0$. With 4-aminobenzoic acid, the emerging supramolecular structure appears to be essentially incommesurate with the initial smectic phase, leading to the depression of $S_A$ together with crystal phase formation.

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