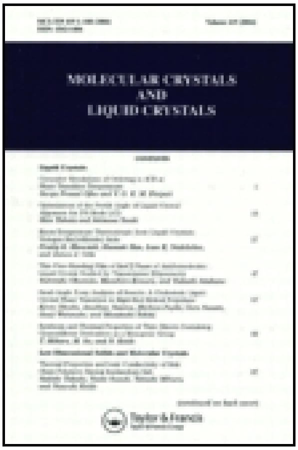

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Effect of Disc-Like Solute Size on the Orientational Order of a Nematogen

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Effect of Disc-Like Solute Size on the Orientational Order of a Nematogen

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We observe that the addition of hexa-*n*-alkoxy triphenylene "disc-like" solutes in a nematic solvent affects the nematic order but that this perturbation is independent of the solute chain length. Some arguments concerning the chain arrangements with respect to the triphenylene ring are proposed.

I INTRODUCTION

In a pure non mesomorphogenic liquid such as $n - C_n$ alkanes the short range orientational order increases with n. Such a behaviour is not revealed in a pure globular molecule liquid such as the highly branched C_n isomers.

In addition, in a mixture of a long chain *n*-alkane with a solute the existence and the importance of correlation of molecular orientations is subordinate to the characteristics of the solute, for example:

1) there is no correlation for a globular solute
2) in a series of $n - C_n$ solutes correlation increases with n
3) and for plate like solutes it increases with their anisotropy.

Numerous depolarized Rayleigh scattering[1–6] and thermodynamic[7–10] studies have provided these results.

The similarities between the long range orientational order in a liquid crystal and the short range correlation of molecular orientations in a long chain *n*-alkane† prompted B. Kronberg *et al.*[11] to investigate the effect of

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† Moreover it is known that the strong nematic order correlations appear only in liquids consisting of molecules which show some characteristics of rigid core anisotropy.[12]

solute size and shape on the nematic order of a liquid crystal compound through in particular two parameters:—the orientational order parameter $S\ (T)$—a parameter β^I connected to the depression of the isotropic—nematic transition temperature:

$$\beta^I = \frac{1 - T^I/T^\circ}{x_s}$$

where T^I is the temperature where the nematic phase first appears on cooling a mixture, T° the isotropic–nematic transition temperature in the pure liquid crystal, x_s the molar fraction of solute ($x_s \leq 0.1$). Both quantities depend on the solute size and shape and they are functionally related:

a) The nematic is the more disorganized ($\beta^I \nearrow$, $S(T) \searrow$) as the globular solute size increases (non correlating solute).

b) In the case of correlating solutes as *n*-alkanes the nematic order is independent of the *n*-alkanes length (β^I = const. $S(T)$ = const.): the solute can correlate its orientations with the anisotropic liquid crystal molecules. Thus, the decrease of the order, which would normally appear and increase with the solute size, is compensated by the increasing of the degree of short range orientational order (between solute and solvent molecules) due to the increase of the anisotropy of the solute with *n*.

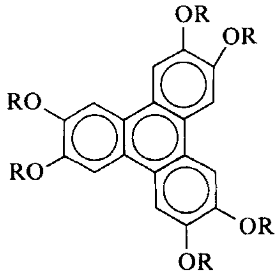
c) In the case of correlating solutes as polyphenyls (non fused rings): these compounds are less flexible than *n*-alkanes and these *rod-like* solutes seem to be better able to correlate with the nematic molecules and indeed orientational correlations between the solute and the liquid crystal increase with the length of the solute. In particular one[13] can observe for the *p*-quaterphenyl solute an increase of the isotropic–nematic transition temperature with regard to the pure liquid crystal, unusual behaviour for a non mesomorphic solute.

We revealed for the first time[14] such a non-classic behaviour in the case of fused rings solutes in several mesomorphic solvents: for instance a highly anisotropic "plate" solute, like chrysene, leads to an increase of the isotropic–nematic transition temperature of a nematic solvent. This increase might be explained by the assumption that these solutes are "virtual" mesomorphic compounds. But in fact this is only an assumption and the solutes we used are not liquid crystal compounds (of course numerous studies concerning the size of the different components of binary mixtures of "rod-like" mesomorphic compounds have been carried out but we shall not quote them here).

On the other hand, after the recent discovery of new thermotropic mesomorphic states with "disc-like" molecules[15–18] it seems to be interesting to know the influence of this type of solute (neither globular nor "rod-like" molecules) on the nematic orientational order.

II EXPERIMENTAL

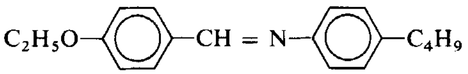
In this paper we analyse the influence of the evolution of the alkoxy-chains length in an homologous series of disc-like molecules, the hexa-alkoxy-triphenylene:[21]



where $R = C_n H_{2n+1}$

$4 < n < 13$

on the nematic order of the ethyloxy benzylidene butyl aniline (E.B.B.A or "204"):



This liquid crystal was used as solvent by B. Kronberg *et al.*[13] in their works, and we choose now the same compound in order to compare the results directly and quantitatively. We present here experimental data obtained by two independent techniques:

1) polarized light microscopy with a FP 5 hot stage which permits to determine the isotropic–nematic transition temperature and thus the β^I parameter; because of small inhomogeneities frequently detected in binary mixtures, it does not seem reasonable to give β^I with more than one decimal.

2) measurement of orientational order parameter through the magnetic anisotropy $\Delta\chi$: these magnetic measurements were performed by the classical Faraday's method discussed in previous papers.[11,12] We take interest in the relative evolution of the orientational order parameter with the nature and the molar fraction of the solute.

Results Because of the lack of molar volume data for all "disc-like" compounds the molar weight is used as a measure of the solute size. The β^I parameter values are indicated in Table I.

TABLE I

Solute	Molar weight g. mole^{-1}	Molar volume cm^3. mole^{-1}	β^I
Triphenylene	228		0.7
"Mesomorphous disc-like"			
$n = 4$	660		1.4
$n = 5$	744	670[22]	1.4
$n = 6$	828		1.4
$n = 7$	912	903[22]	1.3
$n = 8$	996	1016[23]	1.4
$n = 9$	1080		1.3
$n = 10$	1164		1.4
$n = 11$	1248		1.2
$n = 13$	1416		1.2

The β^I value we obtained for triphenylene solute is in good agreement with the studies previously cited.[13] The great difference we observe in the β^I value in the case of triphenylene in comparison with *disc-like* solutes can be explained by the great increase of molar volume (and of course molar weight) due to the addition of six long alkoxy-chains.

But it is essential to emphasize that the length of these chains hardly affect the β^I parameter.

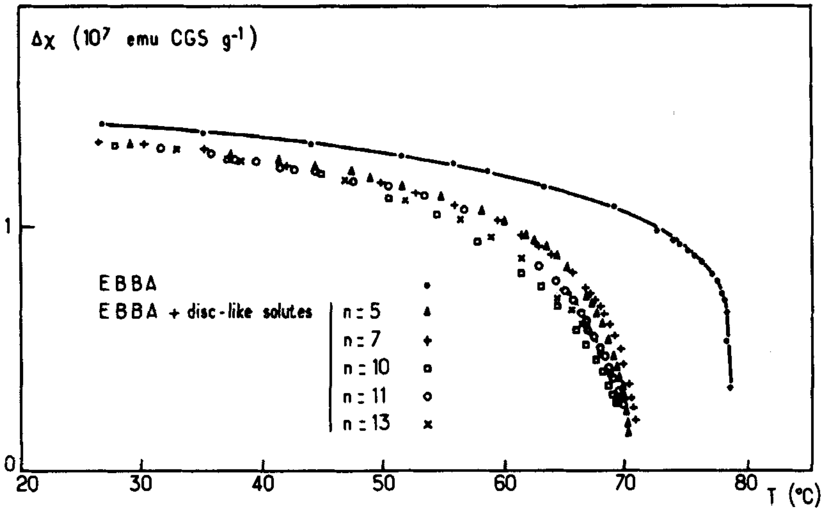


FIGURE 1 Diamagnetic anisotropy (i.e. order parameter S) as a function of temperature for pure E.B.B.A. (●) and mixtures of E.B.B.A. with (n-alkoxy)$_6$ "disc-like" solutes (other symbols).

The behaviour of β^I is confirmed by the comparison of orientational order thermal variations performed on mixtures of EBBA with weak and equal molar fractions of *disc-like* solutes ($x_s \simeq 0.02$) (Figure 1):

a) A decrease of the order parameter at given temperature with respect to the pure compound is observed for all the mixtures.

b) Far from the nematic–isotropic transition range where the nematic order is quasi saturated no significant difference is observable according to the nature of the *disc-like* solute.

Thus we argue that the addition of a (n-alkoxy)$_6$ *disc-like* solute affects the nematic order but this disturbance seems independent of the solute chain length and of molar volume (or weight).

III DISCUSSION

In other words, the previous argument indicates that the increase of the orientational correlations between the *disc-like* solute and the nematic solvent, according to the number of methylene groups in the chains, compensates the increasing disturbance due to the increasing size of the molecule.

These results are analogous to the previously quoted observations concerning the n-alkane solutes: in this case the increase of the solute–nematic correlations with respect to n is to be compared to an increase (with n) of the molecular anisotropy (this one is revealed by depolarized Rayleigh scattering).[1–6] One can suggest by comparison that the anisotropy of the *disc-like* molecules is increased so that the correlations with the nematic molecules are enhanced when the chains are lengthened (spectroscopic measurements should confirm this statement).

Thus in dilute solution with a nematic solvent, the n-alkoxy chains do not seem to be arranged at random with respect to the fused triphenylene rings thereby avoiding a globular shape which is inconsistent with our results.

Moreover the increase of molecular anisotropy also explain in part the increase of short orientational correlations in the liquid phase of pure n-alkanes. By analogy the type of molecular anisotropy we have suggested perhaps remains for pure *disc-like* compounds in their mesomorphous state.

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