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The structure of the nematic phase of cyano derivatives and their mixtures with weakly polar compounds

M. F. Grebyonkin[a]; V. F. Petrov[a]; B. I. Ostrovsky[b]
[a] Organic Intermediates and Dyes Institute, Moscow, U.S.S.R. [b] U.S.S.R. Academy of Sciences Crystallography Institute, Moscow, U.S.S.R.

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The structure of the nematic phase of cyano derivatives and their mixtures with weakly polar compounds†

by M. F. GREBYONKIN and V. F. PETROV
Organic Intermediates and Dyes Institute, Moscow 103787, U.S.S.R.
and B. I. OSTROVSKY
U.S.S.R. Academy of Sciences Crystallography Institute, Moscow 117333, U.S.S.R.

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The nematic phases of cyano derivatives of different chemical classes, in particular pyridine derivatives, and their mixtures with weakly polar matrices, 4,4′-butylmethoxyazobenzene and 4-transbutyl cyclohexanecarboxylic acid, have been investigated by X-ray diffraction over the entire concentration range. Values have been obtained for the fluctuation layer structure period, d, and the longitudinal correlation length, ξ, for two incommensurate density waves corresponding to monomers and dimers of the cyano derivatives. Specific features of the concentration behaviour of d_1 and d_2 depending on the structure of the cyano derivative and the weakly polar matrix have been analysed. A linear correlation between the elastic constant ratio K_3/K_1 and d_2^2 for cyano derivatives has been found, as well as an anticorrelation between K_3/K_1, the viscoelastic ratio, η_s/K_1, and a correlation length, ξ_1, for the mixtures. In the latter case a similar concentration behaviour of η_B/K_3 and ξ_2 and d_2 has been established.

1. Introduction

Determination of the relationship between physico-chemical properties of liquid-crystalline phases and the structural features of their mesogenic molecules still remains a difficult problem. It has been shown, for instance, that comparatively small changes in the molecular structure of a liquid crystal may result in significant changes of its physico-chemical properties [1, 2]. As the liquid-crystalline phase stability is determined by various intermolecular forces, the investigation of intermolecular interactions, association phenomena, dipole–dipole correlations etc. could give a clue to a deeper understanding of liquid crystal properties. Thus, dielectric properties of some polar liquid crystals have been interpreted in terms of antiparallel molecular association [3] which was also involved in the interpretation of elastic properties [4] and of reentrant polymorphism [5]. In nematic mixtures of strongly and weakly polar compounds specific intermolecular interactions leading to the formation of associates allows us to interpret the occurrence of induced smectic phases [6] and to interpret data for viscoelastic properties [7, 8].

The investigation of polar liquid crystals, especially alkyl and alkoxycyanobiphenyls, by X-ray diffraction has revealed not only the existence of a layer structure in the smectic phase of these compounds but also periodic density fluctuations in the nematic phase having a period of d [9–11]. They involve swarms containing

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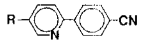
tens to hundreds of molecules and are characterized by a correlation length, ξ, defined directly from the width of the diffraction peak. For the nematic phase of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-heptyl-4′-cyanobiphenyl (7CB) it was shown that the ratio d/L, where L is a molecular length, is about 1·4 [9]. Hence the period of the fluctuating layer structure significantly exceeds a single molecular length, and should be related to the size of the molecular dimer. Such a dimer is formed by two polar molecules being mutually antiparallel. Experimental values of the layer structure period, d, for some other liquid-crystalline cyano derivatives of cyanophenylpyrimidine, cyanophenylcyclohexane and cyanophenylbicyclooctane classes showed that d depends upon the molecular structure of the polar liquid crystal and characterizes in particular the degree of overlap of the molecular cores on dimer formation [12]. Further X-ray diffraction investigations of the nematic phase of polar liquid crystals revealed in some cases the simultaneous existence of two fluctuation layer structures with incommensurate periods d_1 and d_2, where $d_1 < L$ and $L < d_2 < 2L$ [13–15].

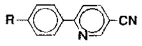
For nematic mixtures of strongly and weakly polar compounds it was found by X-ray diffraction that with decreasing concentration of the cyano derivative the characteristic period of the layer structure, d, decreases and when the concentration becomes less than 50 per cent it is comparable with L [9, 12]. This decrease of d was related to the dissociation of the cyano dimers as their concentration in the mixture was reduced. The concentration dependence of the layer structure periods d_1 and d_2 for the mixtures with cyano derivatives having two incommensurate periods were first studied experimentally in [15]. In [12] a correlation between the concentration dependences of X-ray diffraction intensity and the elastic constant ratio K_3/K_1 (the higher the intensity, the lower K_3/K_1) was revealed. This was interpreted qualitatively using a theory for nematic elastic properties that considered a short range smectic-like ordering of adjacent molecules [16].

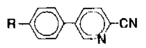
The purpose of this paper is to present a detailed X-ray diffraction study of the nematic structure of various polar compounds and their mixtures with weakly polar compounds. Especially the phenomenon of the coexistence of two incommensurate density waves is considered and a relationship is sought between the X-ray diffraction parameters characterizing the short range smectic-like ordering in the nematic phase and the viscoelastic properties.

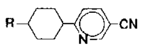
2. Experimental

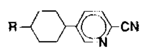
Two and three ring cyano derivatives of different chemical classes were used as polar nematic liquid crystals. Especially the pyridine derivatives:

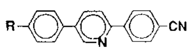

(1Py);


(2Py);

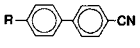
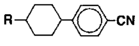
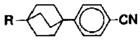

(3Py);

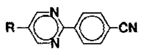
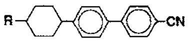

(4Py);

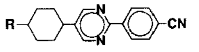
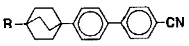

(5Py);


(6Py);

were used where R is $C_5H_{11}-$ or $C_7H_{15}-$. Their chemical names are: 1Py, 5-alkyl-2-(4-cyanophenyl)-pyridine [17, 18]; 2Py, 2-(4-alkylphenyl)-5-cyanopyridine [19]; 3Py, 2-cyano-5-alkylphenylpyridine [20]; 4Py, 2-(trans-4-alkylcyclohexyl)-5-cyanopyridine; 5Py, 2-cyano-5-(trans-4-alkylcyclohexyl)-5-cyanopyridine; 5Py, 2-cyano-5-(trans-4-alkylcyclohexyl)pyridine; 6Py, 2-(4-cyanophenyl)-5-(4-alkylphenyl)pyridine [17, 21]. The physico-chemical properties of the liquid-crystalline pyridine cyano derivatives depend significantly on the location of the nitrogen atom in the molecule, while the geometrical dimensions do not change. In addition, some other well-known cyano derivatives were investigated:

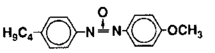
 (CB);  (PCH);  (BCO);

 (Pyr);  (BCH5);

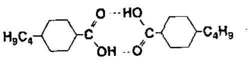
 (RO-CP-7850) 

In most cases the pentyl homologue was used; in the case of PCH the heptyl homologue was used. In those cases when homologue 5 had no nematic phase (for instance, 3Py) or it was necessary to have a wider nematic range, mixtures of homologues 5 and 7 were used in 40 : 60 molar ratio.

Nematic mixtures were investigated with these cyano derivatives as a strongly polar component, and as a weakly polar component:

 (BMAOB)

and

 (CHCA)

were used. Their chemical names and transition temperatures are: BMAOB, 4,4′-butylmethoxyazoxybenzene (T_{CN} = 17°C, T_{NI} = 72°C); CHCA, 4-trans-butylcyclohexanecarboxylic acid (T_{CN} = 47°C, T_{NI} = 93°C). The first compound has been widely used for investigations of viscoelastic [7, 8] and other [25–27] characteristics of mixtures of strongly and weakly polar compounds. The BMAOB molecule consists of two phenyl rings bound by an azoxy bridge with a double bond, so that it can be polarized quite easily. In addition, the BMAOB molecule has a small dipole moment at some angle to the molecular long axis. In mixtures of BMAOB and cyano derivatives this leads to the formation of associates (complexes) of BMAOB and the polar liquid crystal [24, 25]. CHCA consists, both in the solid and the liquid-crystalline states, almost completely of dimers formed of two molecules bound by strong hydrogen bonds. As distinct from BMAOB, it is practically non-polar and has a very weak interaction with cyano derivatives in the mixtures. In addition, the CHCA molecule differs from BMAOB in geometrical size.

X-ray diffraction was performed using an automatic X-ray diffractometer (CoKα radiation, $\lambda \approx 1{\cdot}79$ Å). The primary beam was formed by means of a collimator with input and output slits of width of 0·5 and 0·25 mm, respectively, and a height of 3 mm. Liquid crystal samples of $1{\cdot}5 \times 1{\cdot}5 \times 2\,\mathrm{mm}^3$ were placed between flat electrodes in a thermostated chamber. The liquid crystal was oriented by an electric field of 3 kHz and 1 kV/cm. This proved to be quite sufficient for complete sample orientation due to their large positive dielectric anisotropy. The sample was placed along the goniometer axis such that the counter movement in the recording plane allowed us to scan the nematic reciprocal lattice node along q ($q = 2\pi/d$ is the reciprocal space vector), i.e. in the direction parallel to the director **n**. X-ray diffraction in a wide range of temperatures and concentrations occurred due to smectic fluctuations of either one density wave or two incommensurate density waves. A typical X-ray diffraction profile of the latter type is shown in figure 1. The complicated profile was analysed as the superposition of two gaussians. Thus experimental data for the positions, angular widths and intensities (I) were obtained via a fitting method. The correlation length ξ'' was determined from $\xi'' = \lambda/\Delta(2\theta)$, where $\Delta(2\theta)$ is the angular width of

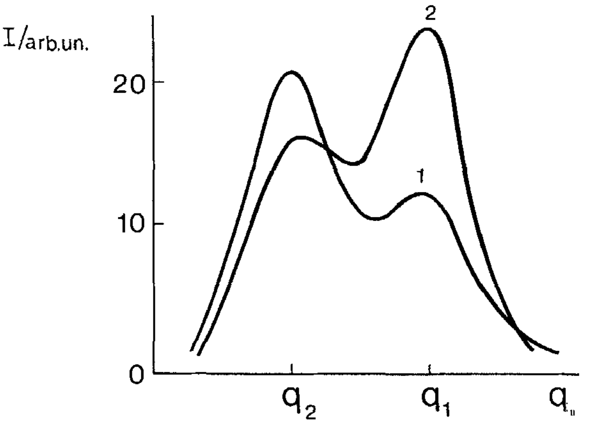


Figure 1. X-ray scattering profile in the vicinity of reciprocal space vectors q_1 and q_2 for the mixture of PCH-7 and BMAOB: (1) PCH-7 concentration is 80 wt %, $T_{\mathrm{CI}}-T = 38{\cdot}5°\mathrm{C}$, $q_1 = 0{\cdot}34\,\mathrm{Å}^{-1}$, $q_2 = 0{\cdot}224\,\mathrm{Å}^{-1}$; (2) $v = 70$ per cent, $T_{\mathrm{CI}}-T = 40°\mathrm{C}$, $q_1 = 0{\cdot}335\,\mathrm{Å}^{-1}$, $q_2 = 0{\cdot}231\,\mathrm{Å}^{-1}$.

the scattering curve measured at half-height. A detailed theoretical description of the X-ray diffraction technique is presented in [15].

Phase transition temperatures were measured by a Setaram III differential scanning calorimeter or by using a polarizing microscope fitted with a heating stage.

To obtain the elastic constants two methods were used. In one case the ratio K_3/K_1 was obtained from the director distribution in a homeoplanar cell, i.e. a cell with uniform planar orientation of the director at one of its plates and homeotropic orientation at the other [26]. In the other case light scattering was used as described in [27, 28]. The experimental geometry was either the B(bend) or the S(splay) mode. The intensity and half-width of the scattered spectrum were used to determine the temperature and concentration dependence of the viscoelastic ratios η_S/K_1 and η_B/K_3 ($\eta_S = \gamma_1 - \alpha_3^2/\eta_2$, $\eta_B = \gamma_1 - \alpha_2^2/\eta_1$), as well as the elastic constant ratio K_3/K_1.

3. Results and discussion

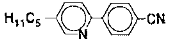
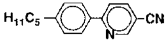
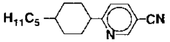
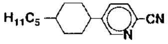
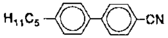
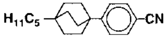
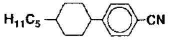
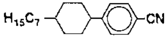
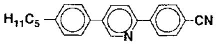
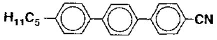
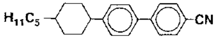
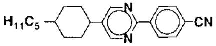
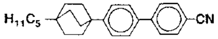
3.1. *Polar liquid crystals (cyano derivatives)*

Table 1 gives the clearing temperatures T_{CI} as well as d_1, l_1, ξ_1, d_2, l_2, ξ_2 for the substances investigated. For comparison some values of d_1 and d_2 for 5CB, BCO-5, PCH-7, 4-cyano-4″-pentylcyanoterphenyl and 4-(4′-pentylbicyclo [2.2.2.]-octyl-1)-4′cyanobiphenyl [12, 13] obtained elsewhere are given in brackets.

For two ring cyano derivatives for some substances only one density wave with a characteristic period d_2 was observed, while for the other substances two (incommensurate) waves with periods d_1 and d_2 are found, d_1 and d_2 being actually temperature independent. Table 1 demonstrates that the first situation is realized for substances having a cyclohexane ring incorporated in the molecular structure.

1Py-5, 2Py-5 and 5CB have similar values of d_1 (15·4, 15·4 and 14·3 Å, respectively). This is quite natural considering that the dimensions of these molecules are practically the same ($L \approx 18$ Å). Thus, the period d_1 should be related to the fluctuation layer structure formed by separate molecules (i.e. the monomeric density wave). In contrast, the d_2 values for the same and other liquid crystals differ significantly (see table 1). This indicates a difference in the characteristic dimensions of the dimers, as for

Table 1. Properties of liquid crystal cyano derivatives of various chemical classes.

No.	Structural formula	Abbreviation	T_{Cl}/°C	d_1/Å	d_2/Å	I_1/arbitrary units	I_2/arbitrary units	ξ_1/Å	ξ_2/Å	
(1)		1Py-5	43·5	15·4	22·7	33	70	42	52	
(2)		2Py-5	68·0	15·4	26·0	30	120	45	66	
(3)		4Py-5	64·0	–	27·3	–	110	–	74	
(4)		5Py-5	55·4	–	24·8	–	80	–	60	$T_{Cl} - T_m = 10$°C
(5)		5CB	35·0	14·3	24·8 (25)	15	70	38	58	
(6)		BCO-5	100·0	(13·2)	24·7 (24·9)				47	
(7)		PCH-5	55·0	–	25.9 (26)	–	35	–	54	
(8)		PCH-7	57·0	–	30 (31)	–		–		
(9)		6Py-5	237	20·5	27·0	100	440	100	130	
(10)		T15	(240)	(20·4)	(30·9)					
(11)		BCH-5	222	20·7	30·7	40	170	70	122	$T_{Cl} - T_m = 100$°C
(12)		RO-CP-7850	231	21·2	26·5	55	250	95	126	
(13)			(270)	(18·0)	(30·7)					

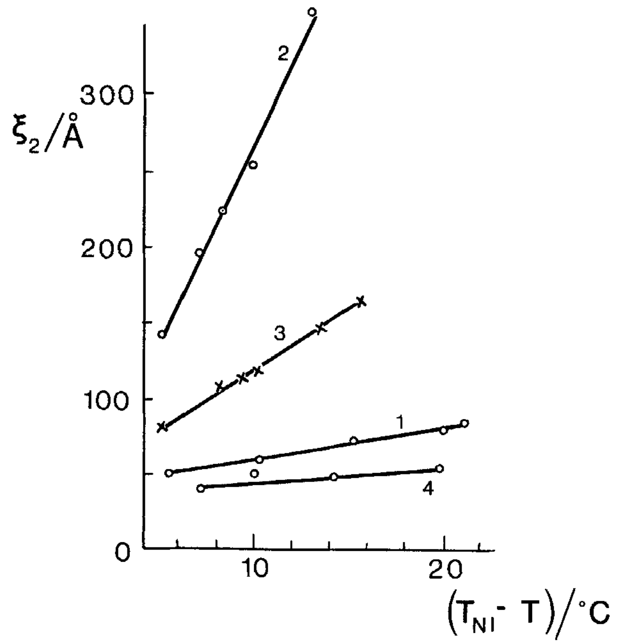
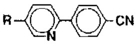
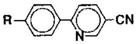
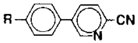
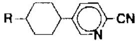
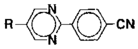
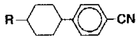
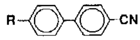
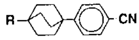


Figure 2. Correlation length ξ_2 versus temperature; (1) 1Py-5,7; (2) 2Py-5,7; (3) 3Py-5,7; (4) Pyr-5,7.

Table 2. Properties of double mixtures (C_5 and C_7) of two ring cyano derivatives.

No.	Structural formula	Abbreviation	T_{Cl}/°C	d_2/Å	I_2/arbitrary units	ξ_2/Å	K_3/K_1
(1)		1Py-5, 7	44·1	25·6	120	63	1·25
(2)		2Py-5, 7	69·1	27·9	475	250	1·11
(3)		3Py-5, 7	49·0	26·6	240	117	1·31
(4)		5Py-5, 7	57·7	27·0	115	69	1·53
(5)		Pyr-5, 7	51·0	23·0	116	50	1·06
(6)		PCH-5, 7	55·1	28·5	52	62	1·68
(7)		5,7CB	39·0	(27·4)			1·37
(8)		BCO-5, 7	96·5	28·2 (27·8)	34	342	1·93

different classes the degree of molecular core overlap in dimer formation is not the same [4, 5]. The different d_2 values probably result from significantly different electron density distributions in the molecular structure (for the pyridine derivatives this is shown in [29]) and steric factors which are responsible for the type of dimerization. In this case we can speak about dimeric density wave.

In order to include cyano derivatives of the 3Py type in the analysis, mixtures of homologues 5 and 7 of various pyridine cyano derivatives as well as cyano derivatives of pyrimidine, phenylcyclohexane and bicyclohexane were studied. The experimental results (T_{Cl}, d_2, I_2 and ξ_2) at $T_{Cl}-T$ of 10°C are given in table 2. The temperature dependence of the longitudinal correlation length ξ_2 is given in figure 2. In investigating the mixtures the monomeric density wave evidence (d_1, I_1 and ξ_1) are somewhat indefinite due to difficulties in the separation of X-ray diffraction profiles corresponding to two density waves and so they are not discussed here. Preliminary experimental d_2 values for homologues 5 and 7 of 2Py had been found to be 26·0 and 29·5 Å, respectively. Then a d_2 value for the 2Py-5,7 mixture was calculated using the additivity rule as 28·1 Å, which almost coincides with the experimental value d_2 of 27·9 Å. This provides a reasonable basis for utilization of data obtained for the mixtures to compare substances of different classes. For 5CB, 7CB and BCO-5,7 mixtures the values of d_2 given in table 2 in brackets were computed by the additive method using the results of [12]. From the data in table 2 it is evident that comparing the mixtures 1Py-5,7 and 2Py-5,7 the same type of correlations is observed as for the homologue 5 of these liquid crystals (1Py-5 and 2Py-5 structures, table 1). The value of d_2 for the 3Py-5,7 mixture proved to be higher than for the 1Py-5,7 mixture, but lower than for 2Py-5,7. Note that for the 3Py-5,7 mixture there is also an intermediate value for the clearing temperature.

For the three ring cyano derivatives of various chemical classes two incommensurate density waves were observed and just as in the case of the two ring compounds d_1 was actually the same for the different substances (see table 1) and corresponded to the monomeric density wave. Except for the lower value $d_1 = 18·0$ Å for 4-(4-pentylbicyclo [2.2.2]-octyl-1)-4′-cyanobiphenyl, in the same way as the value $d_1 = 13·2$ Å for the two-ring BCO-5 [13]. The d_2 value (dimeric density wave) for the 6Py-5 structure is lower than for T15 (d_2 for the two ring pyridine cyano derivative of the 1Py-5 structure is lower than for 5CB). A still lower value of d_2 is observed for the three ring pyrimidine cyano derivative (RO-CP-7850, see table 1), which correlates with the situation noted for the two ring liquid crystals (1Py-5,7 and Pyr-5,7 mixtures, table 2). Comparison of d_2 for the three ring T15, BCH-5 and bicyclooctane derivative (see table 1) shows that their d_2 values are actually the same. Then the major contribution to the interactions in forming the dimer is made by the common molecular fragment that is the cyanobiphenyl group. The molecular cores are overlapped by this particular fragment, while the nature of the third ring (phenyl, cyclohexane, bicyclooctane) does not play any particular role.

Comparison of the data on X-ray diffraction intensities and longitudinal correlation lengths demonstrates (see table 1) that I_1 and ξ_1 are, in all cases, lower than I_2 and ξ_2 (for some substances I_1 and ξ_1 are simply not observed), i.e. for the cyano derivatives studied the dimeric density wave fluctuations are more developed. Then the possible formation of a smectic mesophase at lower temperature must take place with the layer structure period of d_2 rather than d_1. Note, by the way, that on lowering the temperature for 2Py and 3Py a considerable growth of the X-ray diffraction intensity I_2 and the longitudinal correlation length ξ_2 is observed, which testifies to an increased smectogeneity of these classes of cyano derivatives. Similar behaviour is noted for the 2Py-5,7 mixture (see figure 2). This is consistent with the fact that homologues 6 and 7 of these pyridine classes do indeed have a smectic phase.

These features of the nematic phase structure of cyano derivatives belonging to different chemical classes must affect the physico-chemical characteristics of the compounds. A possible correlation with the elastic constant ratio K_3/K_1 seemed to be especially interesting as the latter quantity is an important parameter in defining the slope of the voltage-contrast curve for twisted nematic displays [30]. Table 2 summarizes experimental values of K_3/K_1 for mixtures of the cyano derivative homologues 5 and 7 of different chemical classes at the same reduced temperature $\tau = T/T_{\mathrm{Cl}} = 0·95$ (for 2Py-5,7 $\tau = 0·98$); some values are taken from [17, 26].

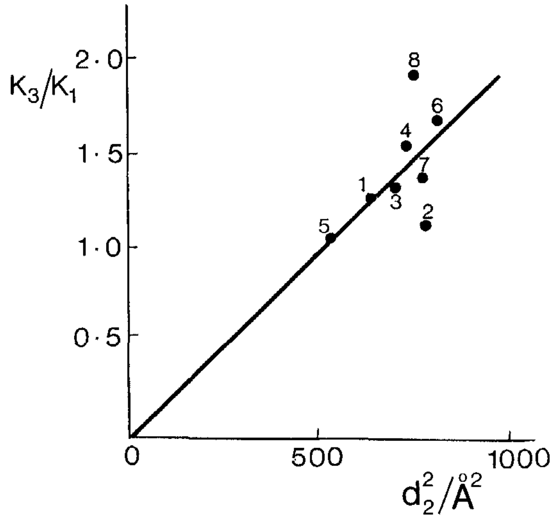


Figure 3. The elastic constant ratio K_3/K_1 as a function of the squared dimeric density wave period d_2^2 for cyano derivative mixtures: (1) 1Py-5,7; (2) 2Py-5,7; (3) 3Py-5,7; (4) 5Py-5,7; (5) Pyr-5,7; (6) PCH-5,7; (7) 5,7CB; (8) BCO-5,7.

In a nematic phase the expression

$$\frac{K_3}{K_1} = \frac{4}{3}\frac{L^2}{W^2}\frac{\langle \mathrm{be}(\alpha)\rangle}{\langle \mathrm{st}(\alpha)\rho^2\rangle}, \tag{1}$$

has been derived for the elastic constant ratio [16] where L and W represent the length and width of a liquid-crystalline molecule, respectively, and the factors $\langle \mathrm{be}(\alpha)\rangle$ and $\langle \mathrm{st}(\alpha)\rho^2\rangle$ characterize the degree of short range smectic-like ordering; K_3/K_1 being reduced with increasing smectic ordering. In order to simplify the analysis, we concentrate first on a situation where purely geometrical factors are of major importance, in which case

$$\frac{K_3}{K_1} \sim \frac{L^2}{W^2}. \tag{2}$$

However for the mixtures investigated the K_3/K_1 ratios are significantly different (see table 2), whereas the geometrical dimensions of the molecules are practically the same (here L and d_1 could be related as seen from table 1), and so equation (2) does not work. But a certain correlation is observed between K_3/K_1 and d_2, the fluctuation dimeric density wave period. This is demonstrated in figure 3 which shows the relationship between K_3/K_1 and the square of the dimeric density wave period d_2^2 (data of table 2), which for the given set of substances is close to a linear function (BCO-5,7 is an exception). In addition, the 2Py-5,7 mixture should be excluded from the analysis, because it is impossible to measure K_3/K_1 at $\tau = 0{\cdot}95$ due to the formation of a smectic phase. Taking W^{D} as the effective width of the cyano derivative dimer (in a first approximation the same for all the cases studied), L^{D} as the effective length of the dimer (proportional to d_2), then equation (2) describes the experimental situation correctly.

To improve the analysis a proper correlation between $\langle \mathrm{be}(\alpha)\rangle$ and $\langle \mathrm{st}(\alpha)\rho^2\rangle$ and the measured values of the longitudinal and transverse correlation lengths [31] representing the size of fluctuation smectic regions must be found. Actually in this way we

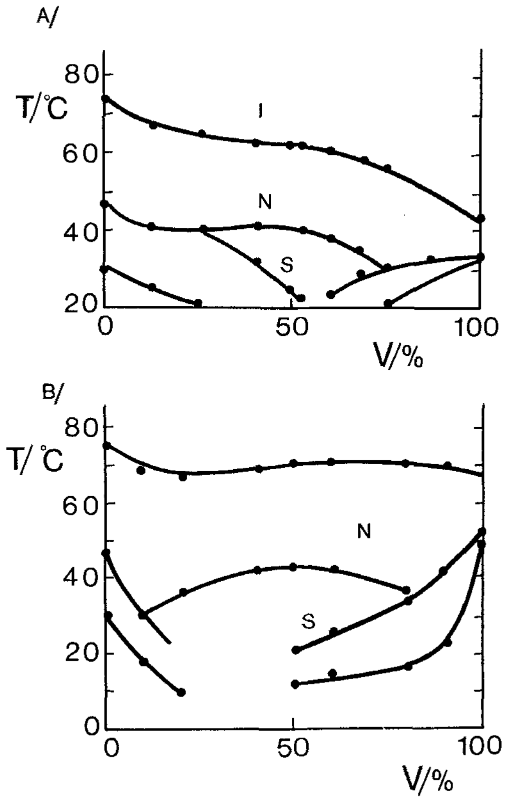


Figure 4. Phase diagrams for the systems (A) 1Py-5 + BMAOB and (B) 2Py-5 + BMAOB.

could explain the deviation of the points for BCO and 2Py from the linear dependence in figure 3. Taking into account the high values of ξ_2 for 2Py (see table 2), characteristic of strong smectic-like ordering, the values of K_3/K_1 for 2Py must be much lower than for the major group of substances having comparable ξ_2 values. The values of ξ_2 for BCO are, in contrast, low (see table 2), resulting in higher K_3/K_1 values. This fact is in a good agreement with the previously found correlation between K_3/K_1 and ln I for different classes of cyano derivatives (here I is the X-ray diffraction intensity which in our case corresponds to I_2). An increase in ln I, representing increasing short range smectic ordering, is accompanied by a reduction of K_3/K_1 [12].

In this interpretation dimers formed by the cyano derivatives play an important role. In combination with the better development of the dimeric density wave as compared to the monomeric one, this proves that for polar liquid crystals the balance in the monomer-dimer system of $2M \rightleftarrows D$ (considering data on the correlation factor [2, 3]) is biased towards dimers.

3.2. *Mixtures of strongly and weakly polar compounds*

The mixtures of strongly and weakly polar compounds considered represent a typical system, where an induced smectic phase is observed. Specific features of its formation depend on both types of compounds. Thus, in the system 5CB + BMAOB the induced smectic phase is observed for a concentration range of $V = 45$–70 wt % (V is a concentration of the cyano derivative in the mixture) at temperatures 30–40°C

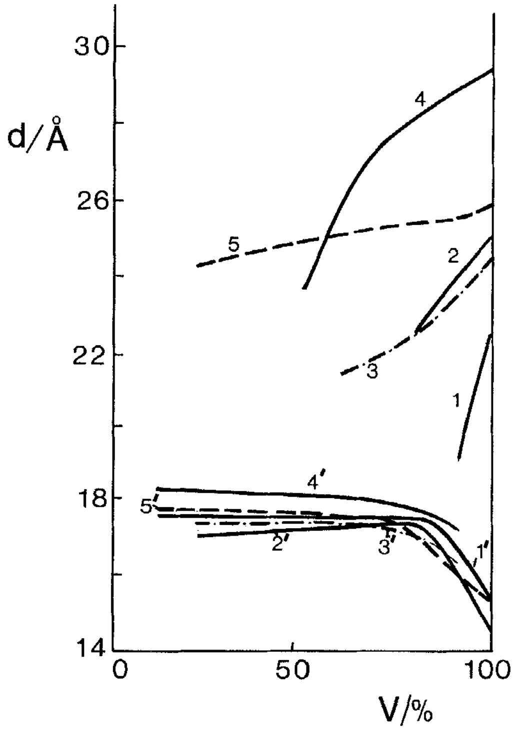


Figure 5. Concentration dependence of the fluctuation layer structure periods d_1 (1'-5') and d_2 (1-5): (1,1') 1Py-5 + BMAOB; (2,2') 5CB + BMAOB; (3,3') BCO-5 + BMAOB; (4,4') PCH-7 + BMAOB; (5,5') 2Py-5 + BMAOB.

below T_{Cl}. The phase diagrams for 1Py-5 + BMAOB and 2Py-5 + BMAOB are shown in figure 4. A clear reduction of the melting temperature and the emergence of a corresponding induced smectic phase are observed at intermediate compositions. However, it must be emphasized that the results refer exclusively to a nematic phase far away from the smectic–nematic phase transition.

The fluctuation layer structure periods d_1 and d_2 measured by the X-ray diffraction versus concentration are shown in figure 5 for various mixtures. As for pure cyano derivatives, in many mixtures the coexistence of two incommensurate density waves is observed. Indeed, for the 1Py-5 + BMAOB system with a high cyano derivative concentration (V = 80–100 per cent), at the same time two fluctuation density waves with incommensurate periods d_1 and d_2 (see figure 5, Curves 1 and 1') are obtained. As the cyano derivative concentration in the mixture is reduced, an insignificant increase in d_1 and rapid decrease of d_2 occur. When the cyano derivative concentration is lower than 80 per cent, the density wave with the d_2 period is no longer observed, and the scattering is localized near the reciprocal space vector corresponding to a density wave with an almost unchanged period d_1. A similar result was obtained earlier for 4-*n*-pentyl-4'-cyanobiphenyl + BMAOB mixture [15] (see figure 5, Curves 2 and 2'). For the BCO-5 + BMAOB (see figure 5, Curves 3 and 3') and the PCH-7 + BMAOB (see figure 5, Curves 4 and 4') systems the density wave fluctuation scattering with the d_2 period is maintained in a larger cyano derivative concentration range ($V \approx$ 55–100 per cent), the value of d_2 being decreased with increasing concentration of the weakly polar component though not so rapidly as for the 1Py-5 + BMAOB and 5CB + BMAOB systems. The d_1 period is not observed for pure

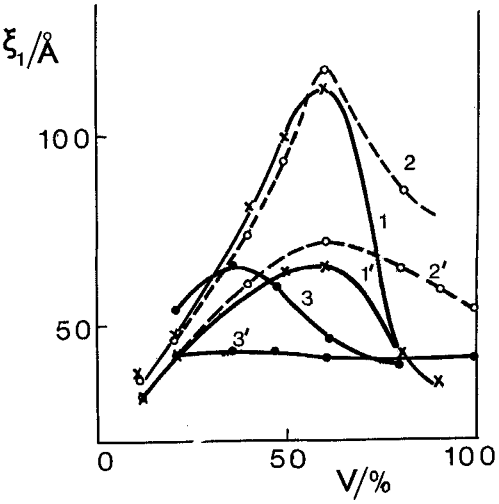


Figure 6. Concentration dependence of the correlation length ξ_1: 1Py-5 + BMAOB: (1) $T_{\mathrm{CI}} - T = 30°\mathrm{C}$, (1') $T_{\mathrm{CI}} - T = 20°\mathrm{C}$; 2Py-5 + BMAOB: (2) $T_{\mathrm{CI}} - T = 30°\mathrm{C}$, (2') $T_{\mathrm{CI}} - T = 20°\mathrm{C}$; BCO-5 + BMAOB: (3) $T_{\mathrm{CI}} - T = 40°\mathrm{C}$, (3') $T_{\mathrm{CI}} - T = 20°\mathrm{C}$.

PCH-7 (as well as for PCH-5) and BCO-5 but already at $V \approx$ 80–90 per cent it does occur and its value coincides practically with those of other systems. We did not succeed in experimental observation of X-ray scattering for pure BCO-5 near the reciprocal lattice vector q_1 corresponding to the period of d_1.

The concentration dependence of d_1 for the 2Py-5 + BMAOB system is similar to that of 1Py-5 + BMAOB and other investigated systems. But the density wave fluctuation scattering with the period d_2 is maintained almost over the entire range of cyano derivative concentrations (V = 20–100 per cent, figure 5, curve 5), the concentration dependence of d_2 being weak.

For the 2Py-5 + BMAOB system within the concentration range V = 80–100 per cent the X-ray scattering intensity I_2 (corresponding to the density wave with the period d_2) is higher than I_1; for lower concentrations the situation is different, I_1 increases while I_2 remains unchanged. For the other systems the situation in the concentration range V = 80–100 per cent is analogous, while at lower concentrations I_2 is rapidly damped. The corresponding concentration dependence of the longitudinal correlation lengths ξ_1 and ξ_2 for the three systems investigated are shown in figures 6 and 7, respectively. ξ_2 decreases monotonically with the concentration of the cyano derivative (see figure 7). The concentration dependence of ξ_1 for all three systems has an evident maximum whose magnitude increases with decreasing temperature. The maximum concentration dependence of ξ_1 is observed at $V \approx$ 60 per cent for 1Py-5 + BMAOB and 2Py-5 + BMAOB and at $V \approx$ 35 per cent for BCO-5 + BMAOB. For 5CB + BMAOB and PCH-7 + BMAOB the maximum is observed at V = 50–60 per cent [15] as well. The magnitude of the maximum at a certain reduced temperature depends on the nature of the cyano derivative. When the temperature drops, ξ_1 and ξ_2 grow (see figure 6, and also [15]), the growth of ξ becoming infinitely large when approaching the phase transition. Thus for mixtures of the cyano derivatives with the weakly polar matrix BMAOB within a certain concentration interval a simultaneous coexistence of two incommensurate fluctuation density waves is observed. The density wave with the period d_2 is again associated with dimers of the cyano compound, at least when V is large. When V approaches the

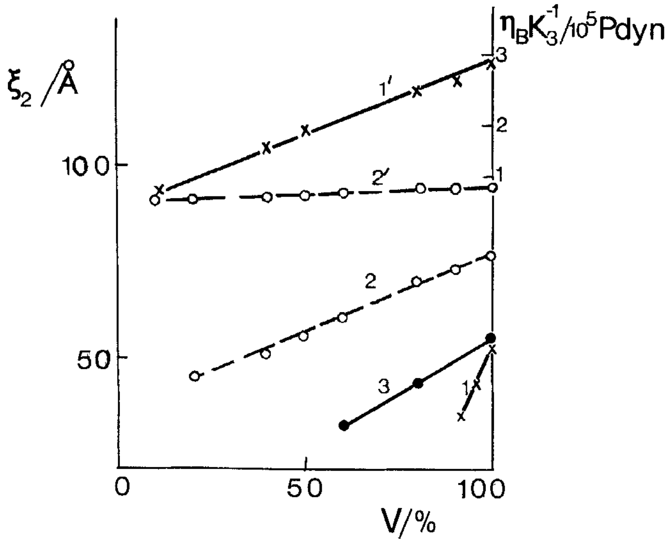


Figure 7. Concentration dependence of the correlation length ξ_2 (1,2,3) and the viscoelastic ratio η_B/K_3(1′, 2′), $T_{CI} - T = 20$°C: (1,1′) 1Py-5 + BMAOB; (2,2′) 2Py-5 + BMAOB; (3) BCO-5 + BMAOB.

middle range and especially low values the molecules of BMAOB must be considered in forming the fluctuation smectic-like layer with the period d_2. The interpretation of the density wave with d_1 is more complicated, as it is associated not only with monomers of the cyano compound but also with the monomers of the weakly polar BMAOB and, moreover, with the complexes formed by these compounds.

Now let us consider the properties of mixtures of strongly polar compounds with the non-polar CHCA matrix. The concentration dependence of the characteristic fluctuation layer structure size is shown in figure 8. A significantly different behaviour of d_1 and d_2 is observed as compared to mixtures of the same cyano derivatives with BMAOB (see figure 5). In fact, for 5CB and 1Py-5, the substances, which mixed with BMAOB display with decreasing concentration a rapid disappearance (at $V \approx 80$ per cent) of the density wave with d_2, show a different behaviour when mixed with CHCA: the density wave with d_1 rapidly disappears (already at $V \approx 90$ per cent), while the density wave with d_2 remains over the entire concentration range. For the PCH-7 + CHCA system a density wave with d_1 is not observed at all, while the density wave with d_2 exists over the entire concentration range; d_2 decreases monotonically from 29 Å to 22·6 Å. In figure 9 the concentration dependence of the correlation length ξ_2 is given for the 5CB + CHCA and PCH-7 + CHCA mixtures. Again we can see the rise of ξ_2 with decreasing the temperature, the maximum being at $V \approx 50$ per cent for the 5CB + CHCA system $V \approx 30$ per cent for the PCH-7 + CHCA system. This demonstrates a growth of the smectic-like ordering at these concentrations.

The X-ray diffraction data (at $V \approx 10$ per cent) yield the following dimensions: for BMAOB ≈ 18 Å and for CHCA ≈ 22·6 Å (for CHCA the hydrogen-bonded dimer size is meant). We suppose that the difference in the molecular size of the two weakly polar matrices investigated is essentially responsible for the different density wave stability. Nevertheless the detailed analysis of this situation is rather complicated

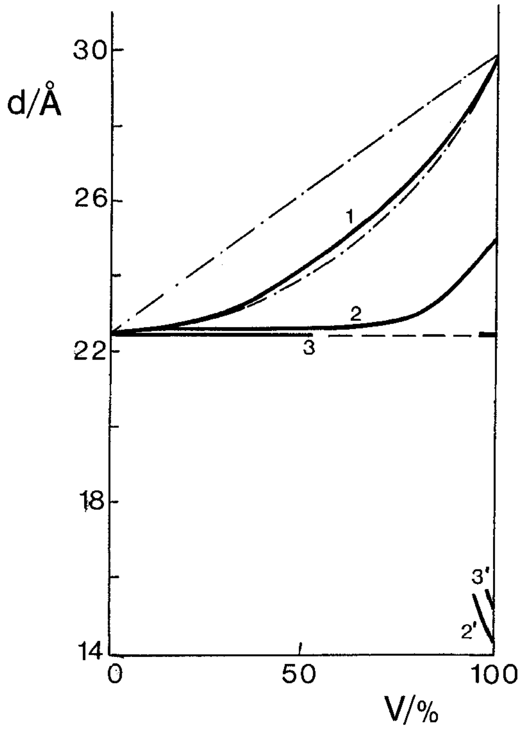


Figure 8. Concentration dependence of d_1(2′, 3′) and d_2(1–3): (1) PCH-7 + CHCA; (2,2′) 5CB + CHCA; (3,3′) 1Py-5 + CHCA.

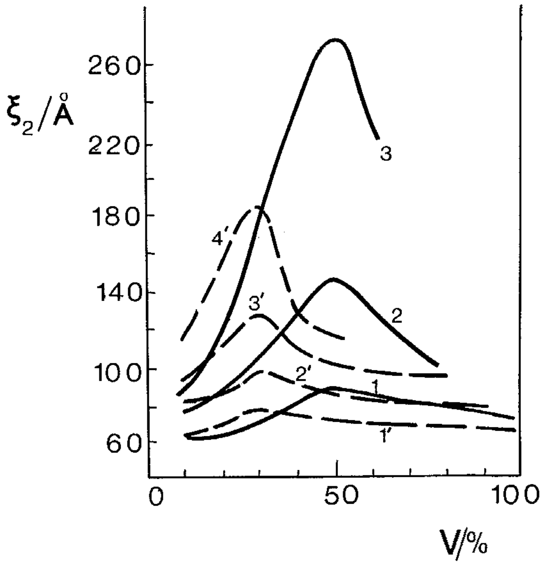


Figure 9. Concentration dependence of the correlation length ξ_2: (1–3) 5CB + CHCA; (1′–4′) PCH-7 + CHCA; (1,1′) $T_{\mathrm{Cl}} - T = 20°\mathrm{C}$; (2,2′) $T_{\mathrm{Cl}} - T = 30°\mathrm{C}$; (3,3′) $T_{\mathrm{Cl}} - T = 40°\mathrm{C}$; (4′) $T_{\mathrm{Cl}} - T = 50°\mathrm{C}$.

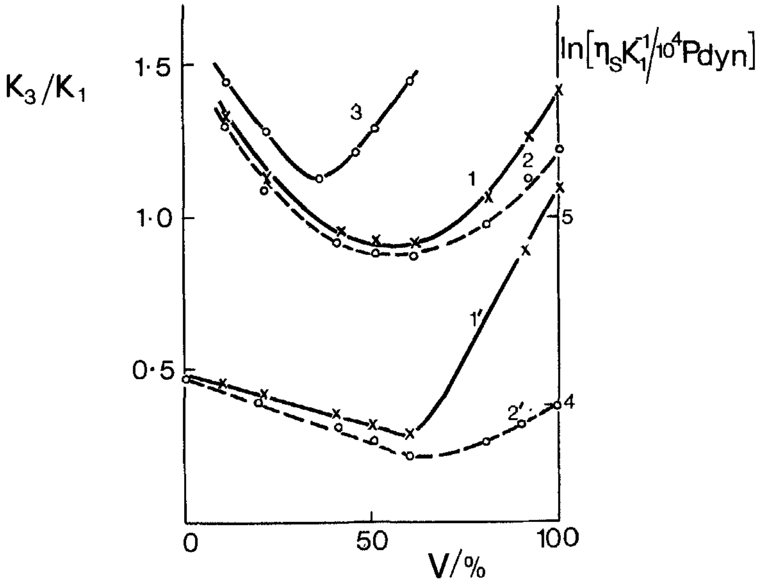


Figure 10. Concentration dependence of the elastic constant ratio K_3/K_1 and the viscoelastic ratio η_S/K_1, $T_{CI} - T = 20°C$; (1,1′) 1Py-5 + BMAOB; (2,2′) 2Py-5 + BMAOB; (3) BCO-5 + BMAOB; (1–3) K_3/K_1; (1′,2′) η_S/K_1.

because of the involvement of such processes as dimerization, dissociation and complex formation.

We now compare the X-ray diffraction characteristics and the viscoelastic properties of the mixtures. In figures 10 and 7 the elastic constant ratios, K_3/K_1, and the viscoelastic ratios, η_S/K_1, and η_B/K_3, are given as a function of concentration. The ratio K_3/K_1 for the pure pyridine cyano derivatives differ insignificantly, K_3/K_1 being higher for the 1Py-5 structure compound. As the cyano derivative concentration in the mixtures is reduced, K_3/K_1 drops, its minimum being at $V \approx 60$ per cent, then it increases again with further reduction of the cyano derivative concentration. For the BCO-5 + BMAOB system the minimum of K_3/K_1 occurs at $V \approx 35$ per cent. As can be seen from figures 6 and 10, higher values of ξ_1 correspond to lower values of K_3/K_1. The results obtained for the concentration dependence of K_3/K_1 do not agree with the conventional concept of the influence of the smectic order parameter fluctuation on the elastic constants of nematics [32]:

$$K_3 = K_3^0 + A\,\xi'', \; K_1 \approx \text{const}, \quad K_3/K_1 \approx \text{const} + A'\xi''. \tag{3}$$

According to this equation, the concentration dependences of K_3/K_1 should have a maximum at the same concentration as for $\xi_1(V)$. The experiment yields the reverse dependence (see figure 6, and also [12]). The result reveals in nematic mixtures of polar and weakly polar liquid crystals a mechanism causing an effective reduction in K_3/K_1, which is probably independent of the possible presence of a smectic A phase at low temperatures and of a pretransitional growth of the smectic fluctuation correlation length. As the K_3/K_1 maximum corresponds to the same concentration values of the mixtures which correspond to a minimum of the ξ_1 value, the implication is that there exists a correlation between an increase in the density wave scattering and a reduction in K_3/K_1. (Here as distinct from [12] owing to simultaneous observation of two incommensurate density waves, particularly for the 2Py-5 + BMAOB system, it is possible to separate the contributions of the densities waves with periods d_1 and d_2 in the observed correlation of ξ and K_3/K_1.) This can be explained in terms of a model with a short range smectic-like molecular ordering in nematics proposed in [16]. According to this concept, between adjacent molecules of a liquid crystal in the nematic phase there can be correlations in their centres of mass in the direction parallel to the director, which do not necessarily result in one dimensional crystallization. These are effects of a much shorter range order, nevertheless leading to a renormalization of the K_3/K_1 ratio, resulting in expression (1). The parameter α represents the relative bias of the centres of waves of the adjacent molecules (for an ideal smectic order $\alpha = 0$). According to [16] an increase in the short range smectic ordering (decrease of α) must lead to a reduction of K_3/K_1 due to the corresponding change of $\langle \mathrm{be}(\alpha)\rangle/\langle \mathrm{st}(\alpha)\rho^2\rangle$. On the other hand, a reduction of α results in a growth of the scattering power of the smectic fluctuation region in a nematic, thus increasing the scattering intensity. According to the law of intensity conservation, this must result in an effective decrease of the scattering curve angular width and increase of the corresponding correlation length. Consequently, here as for the pure cyano derivatives (see §3.1) there is a qualitative agreement of theory with experiment, it seems quite possible that future investigations will reveal a quantitative description of the relationship between the $\langle \mathrm{be}(\alpha)\rangle$ and $\langle \mathrm{st}(\alpha)\rho^2\rangle$ functions and a correlation length describing the short range smectic ordering in a nematic phase.

In this connection some points require further analysis. First of all, the relationship between a short range smectic ordering which is represented by the correlation length, ξ'', and the coupled correlations introduced in the theory [16] is not quite clear. Though a transition from two molecules forming a unit with a double thickness and a length equal to the molecular length, to some form of layer formation of several molecules may seem quite natural, and the fluctuating nature of this formation inevitably results in correlations of the molecular orientation along the director and a growth of ξ''. The connection between the short range smectic ordering in the nematic phase and the long range smectic ordering arising in it when the nematic–smectic transition is approached, is also not clear. If we follow a correlation function (say, ξ_1), then with decreasing temperature it will grow, and from a ten to hundred Ångströms range it will go smoothly to thousands—ten thousands of Ångströms in the pretransitional range. This will be accompanied by an initial reduction of K_3/K_1 with its subsequent drastic increase (see, for example, [7]). This means that at a certain moment the mechanism of the correlation length effecting K_3/K_1 is changed. It may so happen that in the range of low values of ξ'', K_3/K_1 is more affected by geometrical factors, i.e. the L/W ratio with the implication that L and W represent length and width of not just a molecule but a dimer or some general fluctuation-type swarm of several dozens of molecules determining the elastic properties of the nematic phase. Then the reduction in K_3/K_1 observed in this work is related to such a process, while in the range of high values of ξ'' (the pretransitional region) the growth of K_3/K_1 agrees well with the conventional concept of equation (3) [37].

Note that the correlation between K_3/K_1 and the short range smectic-like order in the mixtures investigated is maintained by the fluctuation density wave with the period of d_1. We now recall the results of §3.1, where K_3/K_1 for some pure cyano derivatives was found to be proportional to the interlayer distance, d_2. Then it turns out that already at the cyano derivative concentration in mixtures $V = 70$–80 per cent the density wave with d_1 predominantly affects K_3/K_1. While for pure cyano derivatives the magnitude of K_3/K_1 depends essentially on the interlayer distance, d_2; for mixtures geometrical factors do not play any significant role (d_1 for all systems is approximately the same), the major role being played by the development of the short range smectic-like ordering in the nematic phase.

Analysis of the concentration dependences of the viscoelastic ratios (see figures 4 and 7) shows that η_s/K_1 and η_B/K_3 behave in quite a different way. For the 1Py-5 + BMAOB systems the function $\eta_s/K_1(V)$ shows a minimum at those concentration values $V \approx 60$ per cent which showed a minimum for the function of $K_3/K_1(V)$ and a maximum for the function of $\xi_1(V)$ for the same systems. Thus we can say that the viscoelastic ratio, η_s/K_1 (just as the K_3/K_1 ratio) is strongly affected by the development of short range smectic order on a density wave with period d_1, the influence of the latter on the elastic constant, K_1, being predominant. The ratio η_B/K_3 varies monotonically with concentration (see figure 7). It is not so easy to decide about the correlation between η_B/K_3 and ξ_2 (see figure 7), in particular because for 1Py-5 + BMAOB system ξ_2 is observed only over a narrow concentration range. Anyhow from the data on the 2Py-5 + BMAOB system it is easy to note similar functions $\xi_2(V)$ and $\eta_B/K_3(V)$, the steeper curve of $\xi_2(V)$ for the 1Py-5 + BMAOB system corresponds to the steeper curve of η_B/K_3 for the same system, while for 2Py-5 + BMAOB these relationships are much weaker. We can find a similar concentration behaviour for d_2 and η_B/K_3 for the same systems (see figures 5 and 7).

4. Conclusion

X-ray diffraction investigations of a nematic phase provide information on the characteristic structural dimensions of molecules (d being a monomer or dimer size) and clusters (ξ being the size of a fluctuation smectic-like region). Analysis of these data reveals details of the molecular organization in nematic liquid crystals. For cyano derivatives of different chemical classes, in particular for some new pyridine derivatives, coexistence of two incommensurate density waves with periods d_1 and d_2 corresponding to monomers and dimers has been found. A relationship between d_2, characteristic of a cyano derivative dimer length, and the elastic constant ratio, K_3/K_1, has been established. For mixtures of strongly and weakly polar compounds the existence of two incommensurate density waves has also been demonstrated. The concentration dependence of d_1 and d_2 and a correlation length, $\xi''(\xi_1$ and $\xi_2)$, has been studied as a function of the type of cyano derivative and of the weakly polar matrix. Specifically a system of 2Py-5 + BMAOB has been found for which two incommensurate density waves are observed practically over the whole cyano derivative concentration range. Molecular aspects of the phenomena discovered have been investigated and the significant role of the cyano derivative dimers and the dissociation processes after dilution with a weakly polar component and also of the association of a cyano derivative monomer with molecules of a weakly polar component, have been shown. The experiments reveal a correlation between the growth of local smectic-like ordering on a density wave with period d_1 and a decrease in the elastic constant ratio, K_3K_1, which could be explained in terms of the theory described in [16]. Similar correlations have been found for the viscoelastic ratio, η_S/K_1. For another viscoelastic ratio, η_B/K_3, the concentration behaviour is similar to that of d_2 and ξ_2. Thus, an important influence of the existence in a nematic phase of regions with smectic-like ordering on viscoelastic properties has been shown, which is not directly related to pretransitional phenomena in the vicinity of a nematic–smectic transition.

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