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The relationship between the chemical structure of nematic liquid crystals and their pretilt angles

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About 50 different additives in one or more of three different nematic mixtures have been investigated to clarify the relationship between the chemical structure of the liquid crystal and the pretilt angle on a polyimide surface. The pretilts found for cells have been explained within our recently proposed population distribution model. For compounds with cyano-groups at one end, we find that the in-plane order is governed both by the surface–mesogen interaction and by the relative strength of the intermolecular interactions in the nematic phase. This strength is nearly linear in alkyl chain length for the compounds investigated. Changes in the strength due to variations in the core of the molecules can be calculated easily by using group contributions from the known Parachors. The in-plane order can be treated as a simple product of the contributions from the liquid crystal and from the polyimide. Different polar end groups will give different angles between the surface and the optical axis of the individual mesogens in the first monolayer. The cyano-group gives the highest angle and alkyl groups the lowest. For nitro-compounds the dimers formed are so strongly bound that they do not break up at the surface. Nitro-compounds will thus act as dialkyl compounds. For dialkyl compounds the pretilt angles are dominated by the difference between the chain lengths at the two ends of the molecule.

1. Introduction

We have previously investigated how pretilt angles depend on the structure of the alignment layer [1], the curing and heat treatment of the alignment layer [2], and the bulk properties of the liquid crystal [3]. In the last investigation, it was found that it is impossible to obtain good correlations between the bulk properties of the liquid crystal and the pretilt angles. Clearly specific interactions between the liquid crystal and the alignment layer are important.

There have been previous reports [4, 5] concerning the effect of changes in the structure of the liquid crystal. All previous workers in the field have treated the molecules as long rods, and failed to make the distinction between the pretilt angle measured by the crystal rotation method, which is related to the symmetry of the nematic phase, and the orientation of individual molecules at the surface. We have recently shown that, because the molecules at the surface are fixed rather rigidly, the symmetry of the nematic phase will be broken in a layer close to the surface [6–9]. The orientation of the long axes of the individual molecules (as far as this concept makes sense) and the surface will generally be different from the orientation of the symmetry axis in the bulk of the material.

In this report we show how our population distribution model can be used to explain the relationship between mesogen structure and pretilt, and how the parameters used in the theory can be calculated or estimated.

2. Experimental

Weighed amounts of the liquid crystals were mixed. The mixtures were then heated above the clearing point and shaken vigorously. The heating and shaking were repeated two or three times to ensure thorough mixing. Single components from Kanto Chemicals Co., E. Merck, F. Hoffman-La Roche and Chisso Chemicals were used. The base mixtures were ZLI 1132, ZLI 1237 and ZLI 1602 from E. Merck. We tried to use as high a concentration of the dopants as possible. Dopants that were not soluble in at least 10 wt % were abandoned. Some of the mixtures were supercooled, and in a few cases crystallized after the measurements.

Transition temperatures were measured with a Mettler hot stage using an Olympus microscope. Refractive indices were measured using an Abbé refractometer (Atago 1T).

Polyimide synthesis and cell construction have been described in detail previous [2, 3]. The same rubbing procedures were used for all cells.

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Pretilt angles were measured for 120 μm thick samples, as described earlier [2, 3]. At least two cells were filled with each mixture, and the quoted values are the average pretilt values over three measuring points from each of the cells.

3. Brief description of theory

Barmentlo *et al.* [10, 11], found that there is a distribution of the molecules at the surface in a liquid crystal cell. The angle between the optical axis of the molecules and the surface is rather high. They explained the low pretilt in the bulk of the material as a result of the average tilting of the molecules on the surface. All the molecules at the surface have a high pretilt, but as they point in different directions, the average will be low. Increasing the in-plane order increases the pretilt for the bulk of the material.

We [6–9] suggested that since the molecules at the polymer surface are rather strongly bound, they are not free to rotate; the symmetry of the nematic phase is broken close to the surface. With non-cylindrical molecules we will thus have a splay of the optical axis, even though the mechanical axis stays uniform throughout the cell.

We found that by combining the two explanations we could obtain quantitative agreement between theory and experiment [8]. There is an in-plane distribution of the mesogens at the surface, and the pretilt in the bulk of the material is the average of the tilt at the surface. This averaging process takes place over a surface layer of 0·1–1 μm thickness [6]. The following equation was derived [8]:

$$\beta_{\mathrm{obs}} = a_1[(\beta_0 - \alpha) + \alpha(d^*/d] + \tau \qquad (1)$$

where β_{obs} is the observed pretilt by the crystal rotation method, a_1 is the in-plane order [10, 11], β_0 is the angle between the optical axis of the molecules in the first monolayer and the surface, α is the angle between the optical and rotation axes of the molecules, d and d^* are the thicknesses of the liquid crystal cell and the surface layer, respectively, and τ takes into account any physical deformation of the surface. We intend to show that all our experimental results can be explained by this model.

For thick cells $d^* \ll d$. For polyimide alignment layers it is found that $\tau = 0$. Equation (1) can thus be simplified to

$$\beta_{\mathrm{obs}} = a_1(\beta_0 - \alpha) \qquad (2)$$

for the cells used in this investigation.

For the crystalline polyimides (for example, *s*-BPDA-6) there is a regular surface structure. This regular surface structure can translate into a high in-plane order, and a high in-plane order gives a high pretilt [10, 11].

With amorphous surfaces, the polyimide is much less ordered. Even if the liquid crystals attach equally strongly to the surface, there is less order that can be imposed. The in-plane order will thus be lower, and this gives a lower pretilt. In addition, there are indications that the attachment to the surface is weaker on amorphous surfaces for the cyanobiphenyls [12].

4. Results and discussion

4.1. *Polarity and cyano-groups*

For a moment, let us neglect the difference in α, for example, let us treat the mesogens as linear molecules. We will start with some commercial mixtures. We can treat the differences in the pretilt angle as resulting from differences in the in-plane order (a_1), and the angle between the mesogen and the surface (β_0) due to the different composition of the liquid crystals. With the cyano-group attached to the surface, mesogens with the cyano-group at one end would form a high angle with the surface. Mesogens without cyano-groups would form a low angle—see figure 1.

In figure 2 we have plotted the pretilt angles for several commercially available liquid crystal mixtures as a function of the percentage of the molecules with cyano-end groups. For the crystalline polyimide poly-(hexylene-

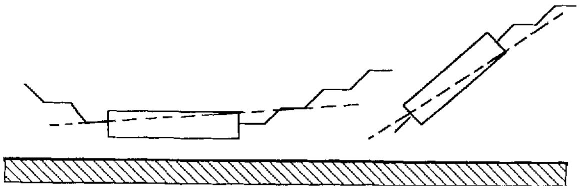


Figure 1. A schematic drawing of the orientation of a cyano-compound and a di-alkyl compound on the surface. The dashed lines indicate their respective mechanical axes.

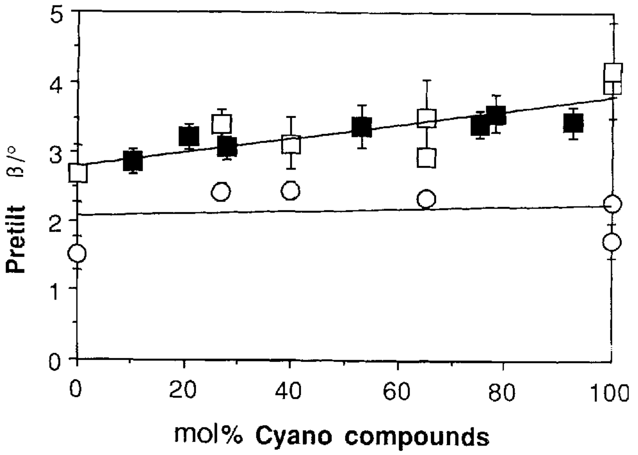


Figure 2. The pretilt angles as a function of mol% of cyano-groups in the mixtures. Open symbols represent different commercial mixtures. Squares on *s*-BPDA-6, circles on PMDA-7. Filled squares are for mixtures of ZLI 1132 and ZLI 1602 on *s*-BPDA-6. The curves are best linear fits to the data.

biphenylimide) (*s*-BPDA-6), there is a clear increase in the pretilt with increasing concentration of the cyano-groups. For the amorphous poly-(heptylene-pyromellitimide) (PMDA-7), the pretilt angle is nearly unchanged.

Also included in figure 2 are the results from a similar experiment with mixtures of ZLI 1132 (four components, all with a cyano-group) and ZLI 1602 (four components, none with a cyano group). Both of these mixtures are based on the phenylcyclohexyl skeleton, and the changes in shape of the mesogens are thus small across this series of mixtures. We see that the results from both sets of experiments fall on the same line, and that there is a linear increase in the pretilt angle with increasing concentration of cyano-end groups. This increase in the pretilt angle can be the result of two different mechanisms in our model. (i) The angle between the surface and the optical axis of the molecule (β_0) may be higher for the cyano-compounds. (ii) The in-plane order a_1 may be higher for the cyano-compounds. We believe that the first mechanism is the dominating one. There are several experimental reasons for this. With the core of the molecule forming an angle of 13–19° with the surface [10–12] for the cyano-compounds, we would expect a decrease in the observed pretilt angle with increasing alkyl chain length, because the angle α increases. As we will see in § 4.3.1., this is what we observe. If the core of dialkyl compounds formed the same angle with the surface, we would expect the observed pretilt angle to decrease also for these compounds, as the alkyl chains gets longer. On the other hand, if the core of the molecules forms an angle of about 0° with the surface, we would expect the pretilt angle to increase, if the longer alkyl chain gets longer. Because the alkyl chain cannot penetrate the substrate, it must in this case point out of the plane, and so move the mechanical axis out of the plane. Increasing the length of the shorter alkyl chain, in the other hand, will lower the pretilt angle for dialkyl compounds, if the core is parallel to the surface. The second situation is what we observe (see § 4.3.2).

Changing the length of the core of the molecules will give the opposite effects. If the cores of the liquid crystal molecules form an angle with the surface, the observed pretilt will increase as the length of the core increases. If, on the other hand, the core is essentially parallel to the surface, any increase in the core length will lower the observed pretilt. An increase is observed for the cyano-compounds (§ 4.4.1), while there is a decrease for the dialkyl compounds (§ 4.4.2). Again we see that the assumption that the cores of dialkyl mesogens are parallel to the surface best accounts for the measurements.

We have previously described how annealing of alkylene polyimides based on PMDA increases the pretilt angle [1, 13]. The annealing increases the order and regularity of the polyimide. Table 1 shows the effect that annealing the alignment layer had on the pretilt angles for some commercial mixtures consisting predominantly of cyano-compounds, and for some without cyano-groups. As can be seen, only the mixtures with a large proportion of cyano-groups showed any increased pretilt. This is probably due to an increased in-plane order (higher crystallinity) of the annealed polyimide [2]. Annealing the alignment layer also drastically reduces the number of defects for ferroelectric smectic C* liquid crystals [14]. Ferroelectric smectic C* materials usually consist of dialkyl compounds. The reduced number of defect for the smectic C* phase thus shows that the in-plane order is increased also for dialkyl compounds. An increase in the in-plane order (a_1), without any accompanying increase in the observed pretilt angle (β_{obs}), can only occur if the angle between the surface and the optical axis (β_0) is near zero.

Table 1. The effect annealing of PMDA-7 on the pretilt angles for several liquid crystalline mixtures.

Liquid crystal	Before annealing	After annealing	Change/per cent
Predominantly cyano-compounds			
ZLI 1237	1·5 ± 0·4	2·0 ± 0·3	+ 33
ZLI 1132	2·3 ± 0·1	2·7 ± 0·2	+ 18
ZLI 3700-000	3·1 ± 0·3	3·8 ± 0·2	+ 23
Predominantly di-alkyl compounds			
ZLI 1081	1·5 ± 0·3	1·2 ± 0·1	− 20
RO-TN-619	3·0 ± 0·1	2·9 ± 0·1	− 3

The only conclusion consistent with all the observations is that the molecules with a cyano-end group prefer to form a large angle with the surface (13–27° from SHG measurements [10–12, 15–17]), while dialkyl compounds prefer a small angle between the core of the molecule and the surface.

Using the Debye equation, it is possible to calculate the polarity of a compound with conformational freedom from known values for the dielectric constants and the refractive indices. This will give an indication of the strength of any dipoles in the liquid crystal.

Table 2 shows data for the refractive indices and dielectric constants for a number of liquid crystal materials. To avoid the problem of these liquid crystals having different order parameters we have calculated the isotropic values

$$x_{\mathrm{iso}} = (x_{\mathrm{para}} + 2x_{\mathrm{perp}})/3, \tag{3}$$

where the subscripts iso, para and perp refer to the isotropic, parallel and perpendicular values, respectively. x is the refractive index (n) or the dielectric constant (ε). The isotropic values were inserted into the Debye

Table 2. Refractive indices and dielectric constants together with calculated polarity for some commercially available mixtures.

	Refractive indexes		Dielectric constants		
Mixture	n_o	n_e	$\varepsilon_{\|}$	$\varepsilon_{\perp}$	Polarity/10^{-29} (J m^3)$^{1/2}$
ZLI 684	1·493	1·700	16·5	5·5	0·813
ZLI 1557	1·499	1·614	7·9	3·7	0·656
ZLI 1602	1·485	1·585	2·77	3·56	0·434
ZLI 1646	1·485	1·565	10·6	4·5	0·756
ZLI 1701	1·499	1·605	8·2	3·8	0·670
ZLI 1800-000	1·481	1·587	11·8	4·8	0·780
ZLI 1800-100	1·479	1·556	7·1	4·2	0·682
ZLI 3700-000	1·485	1·586	16·3	4·8	0·821
ZLI 3497-000	1·495	1·632	28·8	5·8	0·894
ZLI 1132	1·493	1·633	15·0	4·7	0·797
RO-TN-103	1·512	1·735	32·8	7·2	0·897
RO-TN-200	1·534	1·813	26·0	7·7	0·861
RO-TN-619	1·490	1·613	10·6	4·8	0·752
E44	1·522	1·758	22·9	5·2	0·830
ZLI 1081	1·508	1·668	5·5	5·5	0·670
ZLI 1237	1·492	1·632	16·3	5·1	0·817
ZLI 1275	1·484	1·584	3·3	4·1	0·546
ZLI 3102	1·503	1·626	8·4	3·5	0·655
ZLI 3276-000	1·486	1·590	15·9	4·9	0·818
ZLI 3276-100	1·487	1·586	8·3	3·7	0·676
ZLI 3783	1·491	1·591	7·1	3·7	0·644
MJ62738	1·501	1·639	13·2	4·0	0·757

equation, and the polarity calculated. The values are given in the last column of table 2.

From the seven liquid crystal mixtures with known composition we found that the polarity calculated from this procedure agrees with the concentration of highly polar cyano-end groups. Figure 3 shows that the calculated polarity gives a good indication of the composition of the fluids. As the concentration of cyano-groups increases, the increase in polarity decreases. This is as we expect from the preferred anti-parallel ordering of the cyano-groups in dimeric pairs.

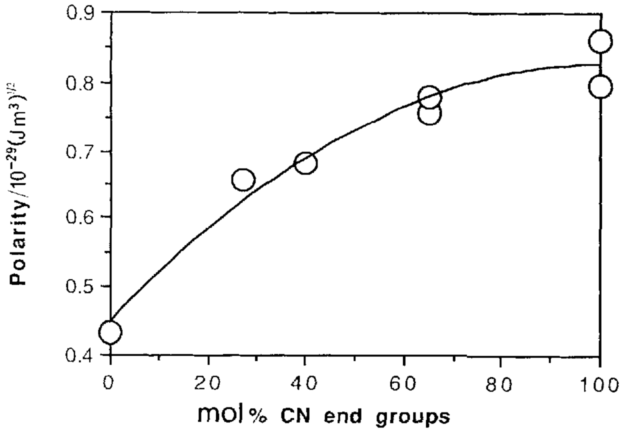


Figure 3. The polarity (10^{-29}(J m^3)$^{1/2}$) of liquid crystalline mixtures as a function of mol % of cyano-groups in the mixtures. The curve is a best second order polynomial fit to the data.

In figure 4 the pretilt angles are plotted as a function of the calculated polarity for a large number of liquid crystal materials investigated previously [3]. We find that there is

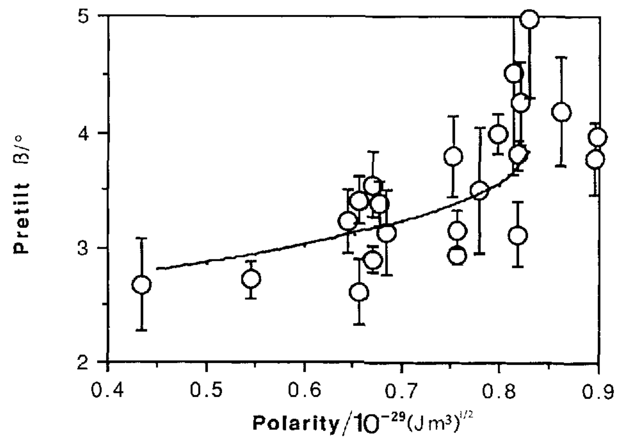


Figure 4. The pretilt angles as a function of the polarity (10^{-29}(J m^3)$^{1/2}$) of commercially available liquid crystalline mixtures on *s*-BPDA-6. The theoretical curve is obtained by multiplying the relationship between polarity and percentage of cyano-groups (from figure 3) with the relationship between the number of cyano-groups and the pretilt (from figure 2). The mixtures and their physical properties used for the calculation of the polarity are shown in table 2.

an increase in the pretilt angle with increased polarity. The increased polarity reflects the fact that we have an increased number of highly polar end groups, mostly cyano-groups. Again, the expected increase in pretilt with more highly polar end groups is found, and thus a higher angle between the surface and the cores of the molecules. The line is drawn by taking the relationship between the polarity and number of cyano-groups (full line in figure 3) and multiplying by the linear relationship between the number of cyano-groups and the pretilt (the full line in figure 2). We see that the difference in the number of cyano-groups explains most of the differences in pretilt angles between these commercial mixtures.

This calculation is of course not able to differentiate between a large number of weakly polar end groups, or a small number of highly polar groups. Even though these two cases would show different interactions with the surface, according to our model, we would calculate the same polarity. The uncertainty in the relationship between the polarity and the structure can thus explain part of the spread of data points from the ideal line in figure 4. Furthermore, we are neglecting any differences in the direction of the dipole within the molecules. But, as we argue that the difference in polarity is mostly due to the difference in the concentration of cyano-dipoles, this effect is small, and all the liquid crystal materials investigated have the cyano-group along the molecular axis.

Our calculations also neglect any differences in average shape of the molecules in the different liquid crystals. We are treating both α, the angle between the optical axis and the rotation axis of the mesogen, and a_1, the in-plane order, as constants, thus adding further spread to our data points. As we will see in § 4.4.1, a higher α is normally accompanied by a higher a_1. The two effects do, at least partially, cancel out. We are also assuming that the angle between the optical axis of the molecules and the surface (β_0) is constant for all the mixtures. This assumption is probably less troublesome. In most cases the cyano-group is along the symmetry axis of the aromatic part of the mesogen, and thus presumably close to the optical axis. As we believe that the cyano-group is interacting with the surface, we will in all cases have the same fragment of the mesogen interacting with the surface. Thus there should be only small differences due to parts of the mesogens further removed from the surface.

As figure 3 shows, there is also a saturation of the polarity. Above 60 mol% of cyano-groups in the mixture, we are not able to find any difference between the fluids. As figure 2 shows, there is, however, a change in pretilt with the number of cyano-groups even above 60 mol%. In the bulk, the cyano-compounds exist in an equilibrium between dimeric pairs and single molecules. Thus, the addition of a cyano-compound to a cyano-rich mixture will hardly change the concentration of free cyano-compounds, and so give no change in the polarity that we calculate. At the surface, the single molecules are bound strongly and the equilibrium is pushed in the direction of free molecules [12]. Hence an increased concentration of cyano-compounds will increase the number of cyano-molecules attached to the surface. We will then observe changes in the surface alignment without changes in the bulk polarity.

By comparing figures 2 and 3, we find that the bulk property of polarity increases roughly as the square root of cyano-concentration, due to the formation of dimers in the bulk. The surface property, pretilt, on the other hand, is linear in cyano-concentration, showing that the dimers are split up at the surface.

4.2. *Variations in the polar end group*

4.2.1. *Additives to ZLI 1602*

As shown in § 4.1., there is a large difference in the orientation between dialkyl compounds and those with a cyano-end group. This prompted us to investigate how different polar end groups affect the pretilt angle. Several different mesogens dissolved in both the dialkyl mixture ZLI 1602 and the cyano-mixture ZLI 1132 were investigated. ZLI 1602 contains mostly alkoxyphenyl-alkylcyclohexanes. This mixture gives rather low pretilt angles on a number of substrates [3]. In this investigation we used only the crystalline polyimide *s*-BPDA-6 which gives a comparatively high pretilt. The variation in pretilt is also larger on surfaces that give a large pretilt and is thus easier to observe on this surface. We added a number of single compounds with only one alkyl chain and different polar end groups to ZLI 1602.

The results are shown in figure 5. The dashed line corresponds to the best fit for the strongly polar cyano-group, as given in figure 2. The horizontal line is the pretilt for undoped ZLI 1602. For additives with a fluoro- or thiocyanato-end group, there were hardly any changes in pretilt over the concentration range investigated. We note that these two groups favour monomer over dimer formation in the bulk liquid crystals. For the strongly polar nitro-group, there was a clear decrease in the pretilt angle, in marked contrast to the behaviour of the cyano-group. The weakly polar aldehyde group, on the other hand, showed nearly the same increase as for the strongly polar cyano-group. It is clear that polarity on its own cannot be the only determining factor.

Attempts to investigate compounds with bromo-, hydroxymethylene or *o*-difluoro-end groups were abandoned because of their low solubility in the host (less than 10 wt%).

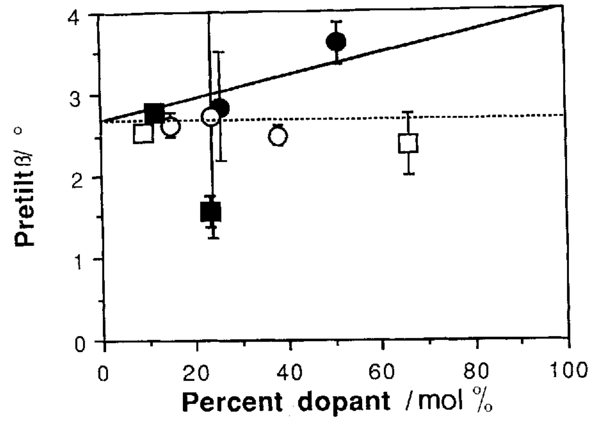


Figure 5. Pretilt angles as a function of the molar concentration for dopants with different end groups in ZLI 1602 with *s*-BPDA-6 as the alignment layer. The full line is the best fit for the cyano-compounds taken from figure 2; the dashed line is the value for pure ZLI 1602. Filled circles, –CHO end group; open circles, –F end group; filled squares, $-NO_2$ end group; open squares, –NCS end group.

4.2.2. *Additives to ZLI 1132*

All components of ZLI 1132 have a strongly polar cyano-group at one end, and this mixture gives a rather high pretilt. As for ZLI 1602, we only investigated the behaviour on the crystalline polyimide *s*-BPDA-6 which gives rather high pretilt. The results are shown in figure 6.

All additives gave a reduction in the pretilt. The reduction was largest for the nitro-group, and smallest for the aldehyde group. The chloro-compound seemed to react with the UV-curable glue used. The cells rapidly turned yellow, first along the end plug, and later over most of the cells. The quoted values were measured within one hour after filling and well away from the end plug.

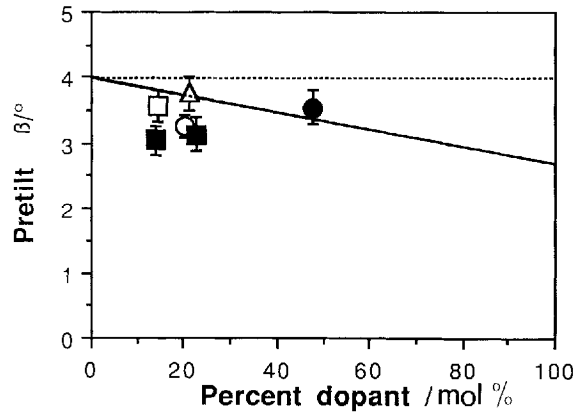


Figure 6. Pretilt angles as a function of molar concentration for dopants with different end groups, in ZLI 1132 with *s*-BPDA-6 as the alignment layer. The full line is the best fit for the di-alkyl compounds taken from figure 2, the dashed line is the value for pure ZLI 1132. Filled circle, –CHO end group; open circle, –F end group; filled squares, $-NO_2$ end group; open square, –NCS end group; triangle, –Cl end group.

Table 3. Properties of the polar end groups in the different liquid crystals investigated. Values are for 4-substituted phenyl derivatives; values in parenthesis are for plain methyl derivatives. The polar end groups are listed in order of decreasing pretilt.

Group	Dipole moment/Debye	Hammett constant	Surface tension/dyn cm^{-1}
–CN	4·18 (3·85)	0·78	39·1 (29·3)
–CHO	2·72 (2·69)	0·22	(21·2)
–Cl	1·69 (1·87)	0·23	17·8 (33·2)
–F	1·60 (1·85)	0·06	
–NCS			41·6
$-NO_2$	4·22 (3·46)	0·66	43·9 (32·3)

The relative order of decrease in pretilt for the additives to ZLI 1132 corresponds with the increase found for ZLI 1602 (for the nitro-group a decrease in both mixtures). We find the following order of pretilt angle for the different terminal groups:

$$-\mathrm{CN} > -\mathrm{CHO} \sim -\mathrm{Cl} > \text{alkyl} \geqslant -\mathrm{F} \sim -\mathrm{NCS} > -\mathrm{NO_2}.$$

This order is the same for both host mixtures. Table 3 lists the different end groups, and some of their relevant properties. The alkyl group is excluded from the list, as steric effects are expected to play a major role for these relatively large end groups.

As we seen from table 3, there are no obvious correlations between the dipole moment of the end group or the surface tension for the comparable substituted benzenes or methyl systems and the pretilt angle. The Hammett constant shows a good correlation, except for the nitro-compound, giving too low a pretilt.

We believe that the nitro-compounds form too strong dimers in the bulk to interact with the surface. The dimers are so strongly bound together that they will not break up at the surface. The nitro-compounds thus act as dialkyl compounds with the same alkyl chain at both ends. As will be shown in § 4.3.2., these dialkyl compounds cause the lowest pretilt angles. The pretilt angle for dialkyl compounds depends on the difference in alkyl chain length at the two ends. A dimer formed by nitro-compounds will effectively have the same alkyl chain at both ends and the difference between the chain lengths is thus zero. In addition, the core of the dimer will have a mirror symmetry, and we cannot point to one end of the molecule as preferred relative to the other. This means that the in-plane order a_1 will be zero. The dimers will thus give the lowest pretilt angles. The difference in alkyl chain lengths will also be zero irrespective of the length of the alkyl chain. The pretilt will thus be independent of the length of the alkyl chain. As shown in § 4.3.3, this is exactly what is found. This can also explain the puzzling fact that the core of a dialkyl compound is found to be nearly parallel to the surface, but still the nitro-compounds give a decrease in the pretilt angle. For cyano-compounds, the competition between dimer formation in the bulk and specific binding to the surface has been observed. The number of monomeric molecules at the surface strongly depends on the surface [12]. Thus, only a slight increase in the forces that hold the dimers together will prevent any binding of the polar group to the surface.

The different end groups give different pretilt angles, and there seem to be both polar and steric effects operating. The cyano-and nitro-groups have about the same dipole strength, but the nitro-group is much larger, and so is sterically hindered from attaching to the surface. The aldehyde group has a negative end and is the same size as the cyano-group. The aldehyde group also gives pretilt angles similar to the cyano-group.

The chloro- and fluoro-substituents are both small and negatively charged. These groups are so small that they are effectively shielded by the hydrogen atoms in the *ortho*-positions of the phenyl ring. In these cases, it is probably more appropriate to consider fluoro-phenyl or chlorophenyl as the groups that attach to the surface. The isothiocyanato-group is long and fairly slim. But as sulphur and carbon have the same electronegativity, there will be no negative charge on the end group, and indeed, due to the electron donating effects of the sulphur, there will be a weak positive charge. Although this compound does not form a dimer and is not sterically hindered, it still gives only a low pretilt angle, indicating that this positively charged group does not attach to the surface.

We thus conclude that a negatively charged group without steric hindrance is needed for the mesogen to attach to the surface, so giving a high β_0.

As we will show in § 4.3.2, dialkyl compounds with an oxygen atom in one of the chains behave as if the methylene groups between the core and the oxygen atom were part of the rigid core. This can also be explained if it is the negatively charged oxygen atom that attaches to the surface.

If a negative group attaches to the surface, we would expect there to be a (slightly) positive site to which it becomes attached. For a fluorine containing polyimide, it has been described how strong rubbing reduces the pretilt angle [18]. As the rubbing stretches and orients the polyimide, we would expect that the in-plane order (a_1) increases. From our model, we would thus expect an increased pretilt with increased rubbing. However, the increased rubbing of a fluorine containing polyimide also leads to fluorine enrichment in the surface layer [18]. In other words, more of the negatively charged fluorines move to the top of the polyimide, while positively charged centres become buried. If this picture is correct, we will have created a hindrance to the attachment of mesogens to the surface. Thus β_0 will decrease. If less of the mesogens attach to the surface, we will also have less break up of dimeric pairs. The dimeric pairs will have one molecular parallel to the rubbing direction and one molecule anti-parallel to the rubbing direction. For dimeric pairs, the in-plane order will thus by 0. More negatively charged fluorines in the top layer will also lower the in-plane order of the first monolayer of liquid crystal, even though the polyimide itself may be better ordered.

There has also been a study showing the effect of the size of the counter ion during polymerization of polypyrrole [19]. This was explained in purely geometrical terms based on the size of the counter ions lying on top of the polypyrrole. It could, in our model, equally well be explained by different distributions of the ions in the polymers and thus a different charge distribution at the surface. More data are needed before the different explanations can be tested properly.

An earlier study [5] has shown that a fluoro-end group in a mesogen gave a lower pretilt than the cyano-group, when different pyrimidines were added to ZLI 3086; that is in agreement with our results.

4.3. *Variations in the alkyl chain length*

4.3.1. *Additions of alkylcyanobiphenyls to ZLI 1237*

Members of the 4-*n*-alkyl-4′-cyanobiphenyl (*n*CB) series were added to ZLI 1237. The resulting pretilt angles on crystalline *s*-PBDA-6 and amorphous PMDA-5 are shown in figure 7. There is a clear decrease in the pretilt when the alkyl chain length increases. There is also a pronounced odd–even effect on the crystalline polyimide. For the amorphous polyimide, both the pretilt angle and the change in pretilt angle are small, and the odd–even effect cannot be seen clearly. The theoretical curves in figure 7 correspond to different shapes of the molecules with the α-values given in table 4. The calculation of the values has been described in detail before [8]. We also assume a linear increase in the in-plane order with increasing number of ethylene ($CH_2.CH_2$) groups in the alkyl chain. The increase per ethylene group corresponds to 20 per cent of the 5CB value, which is in agreement with SHG data [10, 11]. The a_1-value for 5CB in the mixture was taken to be the same as the value for pure 5CB aligned on the same surface.

We also show the results for a series of esters. The theoretical curve assumes the same contribution from the tail for this series as for the *n*CBs. For the contribution from the core, we have fitted all the data, and find that the

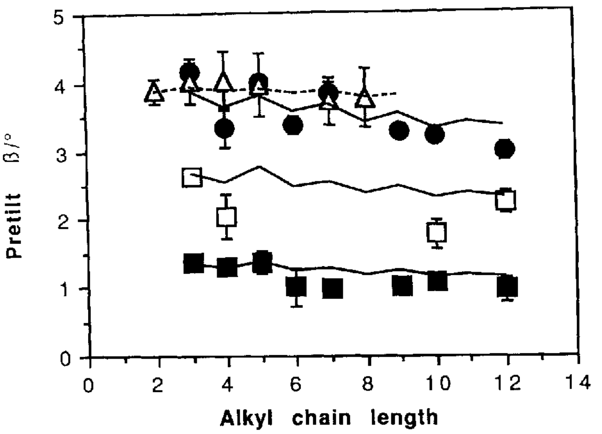


Figure 7. Pretilt angles as a function of alkyl chain lengths for 20 wt% cyanobiphenyl-esters added to ZLI 1237 with *s*-BPDA-6 as the alignment layer (triangles), approximately 40 wt% cyanobiphenyls added to ZLI 1237 with *s*-BDA-6 (filled circles), PMDA-5 (filled squares) and PMDA-7 (open squares) as the alignment layers. The theoretical curves are fitted to pure 5CB for the first two surfaces, and scaled according to the difference between the pretilt of undoped ZLI 1237 on *s*-BPDA-6 and PMDA-7 for the last surface.

contribution from the core is 1·094 times higher than for the cyanobiphenyls. This is used for calculation of the theoretical curve (see § 4.4.1 for more details on the contributions from the core). The cores of these esters are heavier and slightly longer than for the cyanobiphenyls, and the αs are therefore somewhat lower. The values are given in table 4. In all cases, an α of 7° was used for ZLI 1237. The β_0 was found to be 16° by assuming that the a_l-values for ZLI 1237 and 5CB were the same in the mixture as for the pure compounds.

There is good agreement between calculated and measured pretilt angles. Our simplifying assumptions that both the shape (expressed by α) and in-plane order (a_l) can be created as linearly additive quantities seem to work well. There are two competing effects with longer alkyl chains giving both a stronger interaction between the molecules, and thus an increased a_l, and creating a more bent molecule (a larger α). In the cases investigated so far, the effect of the changes in shape is the stronger, and there is a slight decrease in the pretilt angle with increased alkyl chain length.

The assumption that both the shape (expressed by α) and the in-plane order (a_l) can be treated as linearly additive quantities is in many ways related to the mean-field theories for describing the nematic phase. In the mean-field theories, details about the molecules under consideration are included, while the interaction with all other molecules is treated as an average interaction. Mean-field theories have successfully described the orientation of non-cylindrical mesogens in the nematic phase [20], the biaxial orientation of solutes in the nematic phase [21], the conformational distribution and orientation of each conformation of a mesogen in a pure liquid crystal [22], the conformational distribution and orientation of flexible solutes in the nematic phase [23], and the behaviour of dimeric liquid crystals [23]. For the description of a wide range of phenomena, knowledge about all the specific interactions between the different species are not necessary for a good description of the system.

Figure 8 gives the results for a few mixtures of 5CB and 8CB on *s*-BPDA-6. For these two compounds, the relative variations in a_l are known [10, 11]. It has been shown by second harmonic generation measurements on the surface layer that a_l is 20 per cent larger for 8CB than for 5CB [10, 11]. Despite the higher in-plane order for 8CB, we see that the more bent shape more than compensates for this,

Table 4. The shapes of mesogens in five selected series. The structures of the core are shown in figure 14.

Molecule	Shape (α)/°	Molecule	Shape (α)/°
1CB	0·0	PCH1	5·8
2CB	0·9	PCH2	6·0
3CB	1·7	PCH3	6·2
4CB	2·7	PCH4	6·5
5CB	3·9	PCH5	6·7
6CB	5·1	PCH6	7·0
7CB	6·1	PCH7	7·3
8CB	7·3	PCH8	7·6
9CB	8·3	PCH9	7·8
10CB	9·4	PCH10	8·2
11CB	10·2	PCH11	8·4
12CB	11·3	PCH12	8·7
1OCB	0·7	CCH1	5·8
2OCB	1·0	CCH2	6·0
3OCB	1·8	CCH3	6·2
4OCB	2·3	CCH4	6·5
5OCB	3·1	CCH5	6·7
6OCB	3·6	CCH6	7·0
7OCB	4·4	CCH7	7·3
8OCB	5·0	CCH8	7·6
9OCB	5·7	CCH9	7·8
10OCB	6·2	CCH10	8·2
11OCB	6·9	CCH11	8·4
12OCB	7·3	CCH12	8·7
13OCB	7·9		
1PEP	0·0		
2PEP	0·7		
3PEP	1·2		
4PEP	2·2		
5PEP	3·0		
6PEP	4·1		
7PEP	5·0		
8PEP	6·2		
9PEP	7·1		
10PEP	8·2		
11PEP	9·0		
12PEP	10·1		

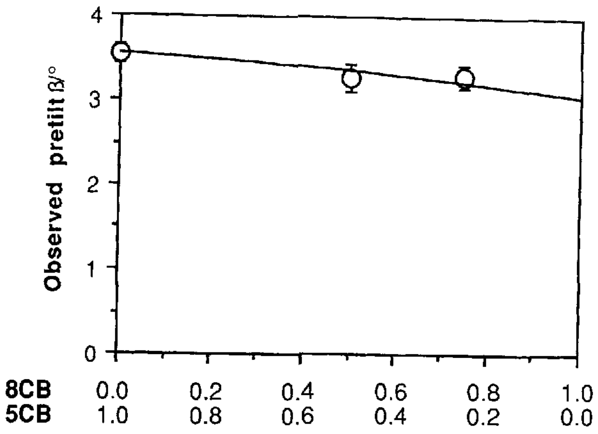


Figure 8. Pretilt angles as a function of the molar composition (mol fraction) for mixtures of 5CB and 8CB on *s*-BPDA-6. The theoretical curve is drawn from the pretilt to 5CB, assuming that the in-plane order (a_1) and shape (α) for the mixtures are the average of the values for the pure compounds.

and we actually find a lower pretilt for mixtures of 8CB and 5CB than for pure 5CB. In this respect the predictions from equation (1) are different from the predictions of [10], and we find that it is necessary also to take the shape of the mesogens into account when attempting to predict the pretilt angle. Since the ratio of a_1 for 5CB and 8CB is known from independent experiments, we also get a better fit between theory and experiment than for the cases where we have to estimate the a_1.

4.3.2. *Additions of dialkyl compounds to ZLI-1602*

Two series of dialkyl compounds were added to ZLI 1602. They are shown in figure 9. The results are similar for the two series. When the longest of the two alkyl chains is increased in length, the pretilt angle increases. When the length of the shortest alkyl chain is increased, the pretilt angle decreases. The results are plotted in figure 9 for the two series as a function of the difference in chain length. When the difference is 0, for example, the same alkyl chain at both ends, the pretilt angles are lowest, and lower than for pure ZLI 1602. When the difference in chain length increases, the pretilt angle increases. The increase becomes relatively smaller as the length of the chains becomes longer. We also note that for the *A* series, substitution of one of the oxygens in the 1′-position with a methylene group give a pretilt that falls nicely on the same curve as the others. For the *B* series, on the other hand, the oxymethylene group needs to be incorporated into the core of the molecule if the data are to fall on the same smooth curve. The exact nature of the interaction between the substrate, the core, and the oxygen atom in one of the chains is not yet understood. It seems as though the slightly negative charge on the oxygen atom fixes this at the surface in much the same way as cyano- or other polar groups are fixed. More is said about this under § 4.4.2. We note that for the different polar end groups, those that are sterically hindered did not seem to attach strongly to the surface. With the oxygen atom in the middle of the alkyl chain, it may of course be somewhat hindered sterically, but it still seems to attach to the surface.

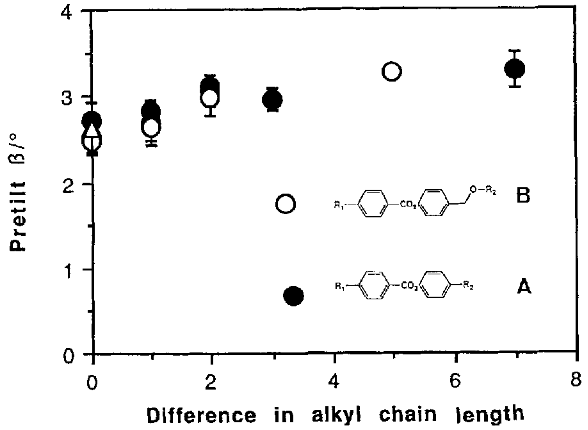


Figure 9. Pretilt angles as a function of differences in alkyl chain lengths between the two end groups for two series of compounds in ZLI-1602. The triangle relates to symmetrical bis(pentylbicyclo-octane).

For addition of cyanobiphenyls to ZLI 1237, the in-plane order (a_1) is found to depend strongly on the length of the alkyl chain. For the dialkyl compounds, we find no such effect. The pretilt angles depend only on the difference between the two chain lengths, and not on the total chain length. If the in-plane order increased with increased chain length, we would expect an increased pretilt angle when the lengths of the alkyl chains at both ends of the molecule were increased. β_0 and α would stay constant, but a_1 would increase.

The dopant bis(*n*-pentylbicyclo-octane), which has a symmetrical core, as well as identical chain lengths, does not give a lower pretilt angle than the members of the *A* or *B* series with series with equal chain lengths at both ends.

The cyano-compounds are only fixed to the surface at one point. Interactions between the mesogens are thus important in determining the in-plane order. For the dialkyl compounds, the cores of the molecules lie (more or less) flat on the surface. There will thus be more interactions between the surface and the mesogens than for the polar compounds. The total interactions are not necessarily stronger, but there will be several points of interaction instead of one. Interactions between the surface and one point in the molecule will only weakly determine the direction of the molecule. Interaction between the surface and two or more points in the mesogen will however stronger determine the orientation of the mesogen.

4.3.3. *Addition of alkyl nitro-esters to ZLI-1602*

The structure of these compounds, as dimers, and the results are shown in figure 10. The filled circles correspond to 10 wt% of the respective compounds added to ZLI 1602. As we can see, the pretilt is independent of the structure of the dopant. The open square corresponds to a mixture of 5 mol% of the ethyl compound and 5 mol% of the decyl compound. The mixture was heated until isotropic (90°C) for 2 h; we expected a possible exchange here: N2–N2 + N10–N10 = 2(N2–N10), where N2 is the ethyl compound and N10 the decyl compound and the dash indicates dimer formation. The resulting N2–N10 has a large difference between the terminal alkyl chains, and we first hoped that this would give a higher pretilt angle. However, as the alkyl chain length is unimportant in determining the in-plane order for dialkyl compounds an increased pretilt could not be observed. Even if the mixed dimers were formed, there would be no preferred direction for the ethyl chains when these mixed dimers attach to the surface. Half of them will point along the rubbing direction, and half against the rubbing direction. The resulting in-plane order (a_1) is still 0.

The N2 and N11 mixtures were supersaturated and the mixtures rapidly crystallized after filling the cell; under the microscope many needle-like crystals appeared. The cell was heated before making measurements and the needles melted or dissolved again. The cells were now completely uniform visually when viewed under the microscope. However, when the pretilt was measured, there was a large spread in the data, and for two points a negative pretilt was found, indicating that the molecules are preferably oriented against the rubbing direction and not along it. After prolonged heating, the pretilt angles became uniform across the cells. These equilibrium values are plotted in the figure. A full account of the new surface memory effect [24] will be given elsewhere [25].

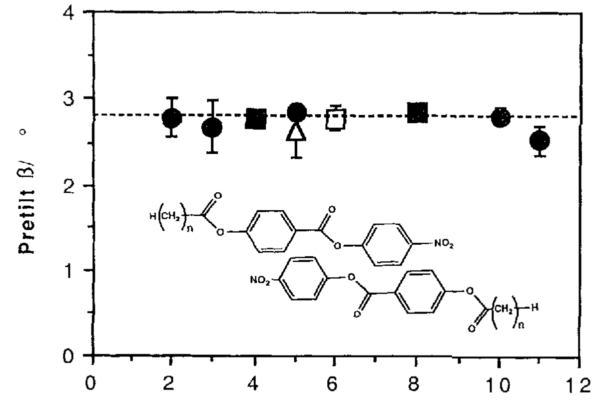


Figure 10. Pretilt angles as a function of alkyl chain lengths for several 4-nitrophenyl esters of 4-alkanoyloxybenzoic acids in ZLI 1602. Filled circles, 10 mol% of the pure additives and open squares, a mixture of 5 mol% of the ethyl-(n-2) and 5 mol% of the decyl-($n = 10$) compounds. Filled squares, 4-nitrophenyl esters with $n = 4$ and 8. The triangle relates to symmetrical bis(pentylbicyclo-octane).

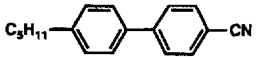
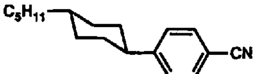
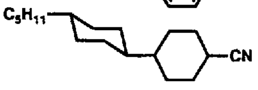
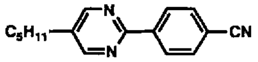
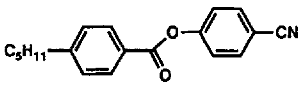
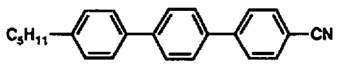
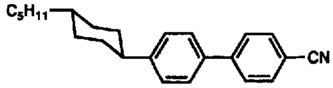
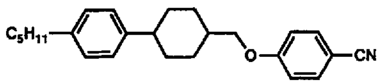
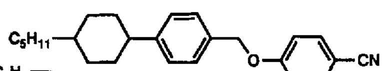
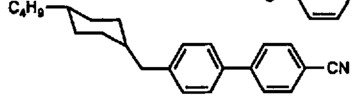
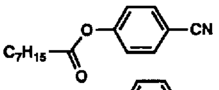
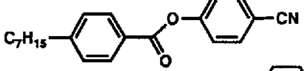
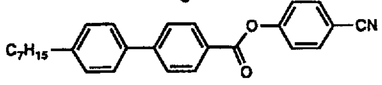
We have also included some structures in figure 10 with shorter or longer molecular cores. These dopants also give the same low pretilt angles. This is consistent with these molecules forming strong dimeric pairs. We thus have a symmetrical strongly bound dimer. As we saw in §4.3.2., molecular with the same alkyl chain length at both ends gave the lowest pretilt. In figure 10, we have also included the value for bis(n-pentylbicyclo-octane); this dopant gives the same pretilt as the nitro-dopants, giving further support to our picture of the nitro-compounds existing as dimeric pairs.

There is a balance between the dimer association and the attachment of the polar end of the mesogens to the surface. For the cyano-compounds, this balance is pushed in the direction of surface attachment. For the nitro-compounds, it is pushed in the direction of dimer formation. There are two possible explanations for this. (i) The nitro-compounds could form stronger dimers in the bulk. (ii) The nitro compounds could be more loosely bound to the surface.

There are data showing that cyano- and nitro-compounds behave differently. Cyano-compounds sometimes form re-entrant phases, while the analogous nitro-compounds do not [26]. Some re-entrant phases are explained by the mesogens melting into a system of strongly bound dimers forming smectic A and nematic phases. Further heating breaks the dimers and a smectic A phase composed of monomers appears, and finally a nematic phase composed of monomers might appear. Smectic A phases of nitro-compounds also have a layer spacing longer than the molecular length [27], indicating dimer formation. The absence of the re-entrant phenomenon suggests that the dimers do not split up at higher temperature, because the dimers are bound more strongly together.

Nitro-compounds also have a higher threshold voltage than the corresponding cyano-compounds, and a much lower temperature dependence of the threshold voltage [28]. A stronger dimer will give a cancellation of the dipolar contribution to the dielectric anisotropy, and thus a lower dielectric anisotropy. This can explain the higher threshold voltage. If the association is strong, there will also be little change in the dimer–monomer equilibrium with temperature, giving smaller changes in the dielectric anisotropy, and thus also in the threshold voltage. There are therefore several arguments in favour of a stronger dimeric association for nitro-compounds than for cyano-compounds.

Table 5. Dopants investigated in ZLI 1237. The table gives the structures, the concentrations (mol %) used, and the shape (α). The calculated pretilts are obtained by scaling a_1 for the core relative to 5CB for the *s*-BPDA-6 surface. Details of the calculations are given in the text. The comparison between theory and experiment is shown graphically in figure 12.

Compounds	Abbreviation	Concentration/mol %	Shape/°C	β_{calc}/°	β_{obs}/°
	5CB	100	3·9		3·53
		40	3·9	3·79	3·98
	PCH-5	25	6·7	3·59	3·63
	CCH-5	25	6·7	3·65	3·86
	CP-5	20	3·9	3·75	3·65
	E-5	20	3·0	3·94	3·73
	T15	10	1·0	3·93	3·88
	BCH-5	10	2·0	3·91	3·97
	5-118-CN	10	15	3·32	3·24
	5-117-CN	10	15	3·32	3·17
	NKV-083	10	20	2·13	2·73
	FC-7	10	25	3·18	2·77
	E-7	10	5·0	3·85	3·59
	BE-7	10	3·0	4·22	3·84

There are also arguments in favour of a weaker attachment to the surface. The nitro-group is larger than the cyano group and thus it will be sterically more difficult to attach to the surface. We refer back to the discussion under § 4.2.2 for the importance of this steric effect.

4.4. *Changes in the molecular core*

4.4.1. *Additives to ZLI 1237*

The Schiff's base mixture RO-TN-200 and the phenylcyclohexane mixture ZLI 1132 gave nearly the same pretilt angles. Both have a cyanophenyl group at one end of the mesogen and a short alkyl chain at the other, whereas the molecular cores are rather different. Also from figure 2 we have seen that the pretilt angle shows a good correlation with the number of cyano-end groups, irrespective of the structure of the rest of the molecules. This gives some indication that the core of the molecule plays a minor part in determining the pretilt angle. We investigated this further by dissolving several mesogens with a cyano-group at one end and a pentyl chain at the other end in ZLI 1237.

The dopants used are listed in table 5 where the concentration (mol %) used for the different compounds, the angle α calculated for each, and the pretilt angles predicted and found are given.

The different cores have two different effects. First, they have a geometric effect, as they have different shapes. There are a few points worth noting when assessing the

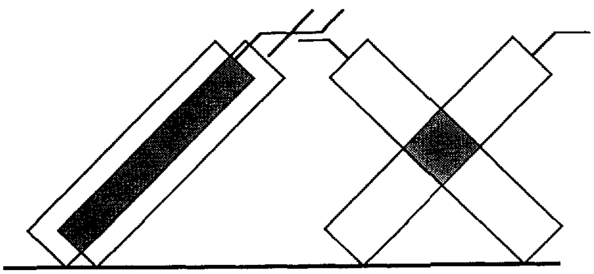


Figure 11. A sketch showing how two molecules attached to the surface in a parallel fashion show good overlap and hence strong interactions, while two molecules attached anti-parallel show smaller overlap.

shapes of these molecules. First, there is nearly free rotation around the bond joining the two cyclohexane rings in CCH-5. For the bicyclohexyl there is a 1 : 1 mixture of the *trans*-conformation with both cyclohexane rings 'coplanar' and the *gauche*-conformation with the two rings at an angle of about 60°, in both the isotropic liquid and the liquid crystalline phase [29]. Also the phenyl–cyclohexyl bond has a small barrier to rotation. In the nematic phase, the most extended conformation will be preferred, and this applies not only to the tail, but also to the core of the molecule.

In our picture we have a situation where the molecules lie mostly along the rubbing direction, and somewhat fewer against the rubbing direction. Assuming thermal equilibrium, the number of molecules with each orientation is dependent on the energy difference between the two orientations. In addition to the surface–mesogen interaction there will be an effect from the forces between the mesogens. Figure 11 illustrates two possible orientations of neighbouring molecules. To the left in figure 11, both molecules point in the same direction (along the rubbing), and the attraction between the two molecules is large, since they roughly overlap over the whole length. To the right one of the molecules is oriented antiparallel to the rubbing direction. There is now very little overlap and thus only a small attractive force.

We start by defining two energy differences. ΔH_{pl} is the energy difference between molecules attached parallel and anti-parallel to the rubbing direction due to the interaction between the polymer and liquid crystal. ΔH_{l} is the energy difference between mesogens having maximum and minimum overlap. We note that the in-plane order can be expressed as a function of the distribution on the surface

$$a_{\mathrm{l}} = (c_0 - c_\pi)/(c_0 + c_\pi) \qquad (4)$$

where c_0 is the number of mesogens parallel to the rubbing and c_π is the number antiparallel to the rubbing. Let us now consider the case where there is thermal equilibrium. The distribution of molecules follows the Boltzmann's distribution, and the dominant interaction is between the polar end groups and some site on the surface. Let us take one molecule and flip it 180° around the surface normal. If the surface layer is perfectly ordered (all molecules according to the right hand side of figure 11), this means breaking the attractive forces between neighbouring mesogens, and not forming any new ones. This will carry a penalty energy-wise. On the other hand, if the initial situation on the surface is random, there will be no energy penalty. We will reduce the attraction to a number of neighbouring molecules by flipping one, but after flipping, we will regain attraction by aligning with molecules of the opposite orientation. If the situation on the surface is random at the start, there will be the same number of favourable attractions after the flipping process as before, and thus no energy difference. For intermediate situations with partial order at the surface, it is easily seen that the chances of breaking and forming attractive bonds to neighbours is exactly the same as the distribution on the surface initially. Thus the energy penalty of flipping one molecule depends on the initial distribution.

The ratio c_π/c_0 is determined by the energy difference between the two states:

$$c_\pi/c_0 = \exp\left[(-\Delta H_{\mathrm{pl}}/kT) - P(\Delta H_{\mathrm{l}}/kT)\right], \qquad (5)$$

where P is the probability of a molecule overlapping well with its neighbours.

We are interested in the ratio of a_{l} for different liquid crystals. We thus combine equations (4) and (5), and substitute a_{l} for P

$$\begin{aligned}&[(1 - a'_{\mathrm{l}})/(1 + a'_{\mathrm{l}})]/[(1 - a''_{\mathrm{l}})/(1 + a''_{\mathrm{l}})]\\ &\qquad = [\exp(-a'_{\mathrm{l}}\Delta H'_{\mathrm{l}}/kT)]/[\exp(-a''_{\mathrm{l}}\Delta H''_{\mathrm{l}}/kT)], \qquad (6)\end{aligned}$$

where the primes and double primes refer to two different liquid crystals. We have assumed that the interaction between the identical polar end groups and the surface is the same in all cases; a_{l} is largely due to the difference in the surface mesogen interaction. We can thus simplify the right hand side of equation (6) by setting $a'_{\mathrm{l}} = a''_{\mathrm{l}} = a_{\mathrm{l}}$. We will also let $1 + a'_{\mathrm{l}} = 1 + a''_{\mathrm{l}} = 1 + a_{\mathrm{l}}$. We have already assumed that ΔH_{l} is small, and therefore we can expand the right-hand side in a series and only keep the first term. Introducing these simplifications and solving for a_{l} we obtain

$$\begin{aligned}&a'_{\mathrm{l}}(a_{\mathrm{l}}\Delta H''_{\mathrm{l}}/kT - 1)\\ &\qquad = a_{\mathrm{l}}(\Delta H''_{\mathrm{l}} - \Delta H'_{\mathrm{l}})/kT + a''_{\mathrm{l}}(a_{\mathrm{l}}\Delta H'_{\mathrm{l}}/kT - 1). \qquad (7)\end{aligned}$$

We have already assumed that both the energies involved are small, so certainly the difference between them is very small. We can thus neglect the first term at the right hand side, to obtain our final equation

$$a'_{\mathrm{l}} = a''_{\mathrm{l}}\left[(a_{\mathrm{l}}\Delta H'_{\mathrm{l}}/kT - 1)/(a_{\mathrm{l}}\Delta H''_{\mathrm{l}}/kT - 1)\right], \qquad (8)$$

where the term inside the bracket is a constant for any given temperature. We see that equation (8) gives a theoretical basis for the constant ratio between the a_1-values of 5CB and 8CB reported previously [10, 11].

We saw earlier that the attractive forces between the tails could be calculated from the number of ethylene groups in the tail [8]. We now turn our attention to how to estimate the attractive forces between the cores of the molecules. The equilibrium constant for dimer formation will give one measure of the intermolecular attraction, but unfortunately only a few equilibrium constants have been determined. Cohesive energy, boiling point, or the surface tension are other measures of the strength of molecular interaction. None of these quantities is directly available to us, but the surface tension can be estimated with good accuracy using the Parachor ($[P]$) [30]. The Parachor is an additive quantity and can easily be calculated for the different cores

$$\sqrt[4]{\gamma} = [P]/V = [P]\delta/M, \qquad (9)$$

where $[P]$ is the Parachor, γ is the surface tension, V is the molecular volume, M is the molecular mass and δ the density of the phase.

Using group contributions to predict properties of liquid crystalline systems is not new. Group contributions have been successfully applied for the description of the order parameters of chlorobenzenes [31], fluorobenzenes [32] and anthraquinones [33] in nematic solvents, as well as the odd–even effect in the nematic to isotropic transitions for alkyl-and alkoxy-azobenzenes [34]. By using group contributions to calculate molecular properties, we are assuming that any atom or bond gives the same contribution irrespective of position in the molecule. This is strictly true only for a few properties (like molecular mass), and fails dramatically when specific interactions like hydrogen bonds are involved. By using the Parachor for calculated the surface tension, an accuracy of 2 per cent is expected [30]. In this work we are not very concerned about the absolute value of the molecular interaction, but more with the relative strength over a series of related compounds.

A larger molecule will have a larger Parachor, as we add contributions from more groups, but this molecule will also occupy a larger volume. The interactions are thus not necessarily stronger. To correct for this fact, we should correct for the molecular volume, at the surface. We should compare $[P]/V$ or $[P]\delta/M$. The densities of our systems are unknown, and as the structure is disturbed at the surface, the density here will also be slightly different from the bulk value. On the other hand, all the systems are fairly similar. We thus ignore the small differences in density and use the specific Parachor (this amounts to assuming $\delta = 1$ for all cases). There has already been an investigation showing a relationship between the surface tension and the pretilt angle for several systems [35].

For 5CB we know that 40 per cent of the a_1-value can be attributed to the core (and 20 per cent to each of the odd numbered methylene groups). We see that some of the other cores have larger specific Parachors, and others have smaller values than the CBs. We scale the a_1-values for these cores by the same amount, giving an a_1-value for each compound. Together with the angle α and the concentration given in table 5 we can then calculate expected pretilt angles for the different mixtures. Examples of this calculation are shown in detail in § 4.5. The comparison between the calculations and the experiments are shown in figure 12. There is a very good agreement. For the base mixture ZLI 1237 the same values for a_1 and α are used as before, and β_0 is also the same. For the ester compounds, particularly those with a seven carbon tail, we seem to overestimate the pretilt, slightly. The reason for this is unknown, but could have something to do with the relatively strong transverse dipole disturbing the parallel ordering.

The interactions between the different cores can be estimated well by using the specific Parachor. Trying to treat the tail in the same way, we run into problems. One of the reasons for this is probably that the Parachor was originally developed for isotropic solutions. In the ordered nematic phase, steric factors play a much more important role between the alkyl chains. For the cores these steric factors are (to a large extent) taken into account by the large correction factors for ring structures and double bonds when calculating the Parachor.

The group at Dainippon Ink [4] found that tolanes were more effective than other two ring compounds in increasing the pretilt for their system. We find that not only is the core longer for the tolanes than for other two ring additives, but also the specific Parachor is higher. The two effects thus contribute in the same direction. For the three ring compounds they investigated, we have calculated that the specific Parachor varies by 3 per cent. The more bent

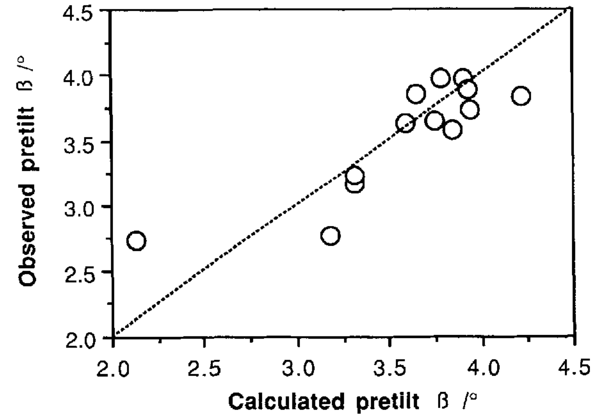


Figure 12. A comparison between the theoretical pretilt angles and experimental results for several mixtures. The compounds and relevant parameters are shown in table 5.

shape resulting from the alicyclic centre ring thus dominates, and as expected they find that liquid crystals with two adjacent phenyl rings give higher pretilts than those with two cyclohexyl rings. Details on the polar end group are not given in the report [4], and a more detailed comparison between their experiments and our model can not therefore be undertaken.

Another report [5] looks into the effect of different two ring cores. The saturated dioxan group seems to give a surprisingly high pretilt, but the alkyl chain lengths are not given. With the large relative contributions from the tail of the molecule, it is not therefore feasible to discuss these results in detail.

4.4.2. *Additives to ZLI 1602*

Figure 13 gives the structures of the dopants and the resulting pretilt angles as a function of the length of the core. We have used molecules with an ethyl chain at one end and a pentyl chain at the other. If these molecules lie flat on the surface, we would expect a longer core to result in a lower pretilt. This is also what we find. As we saw under § 4.3.2, any oxygen atom in the chain means that the alkylene group between the oxygen atom and the nearest ring must be included in the core of the molecule. This clearly shows that the slightly negative oxygen atom is rather firmly fixed to the surface, in much the same way as the strongly polar end groups. With the oxygen atom and the rings fixed, the alkylene groups in between have lost their freedom to adopt different conformations and must be regarded as part of the rigid core.

5-PCH-O2 gives the highest pretilt. For the oxygen atom to attach to the surface in this molecule, it will have to be *gauche* to two of the methylene groups in the ring. This is sterically unfavourable. For this molecule, it might be better to regard the oxygen atom as part of the chain. This will give us a seven membered chain instead of the five membered chains for all the other compounds. As we saw in § 4.3.2, the pretilt increases when the difference in chain length increases.

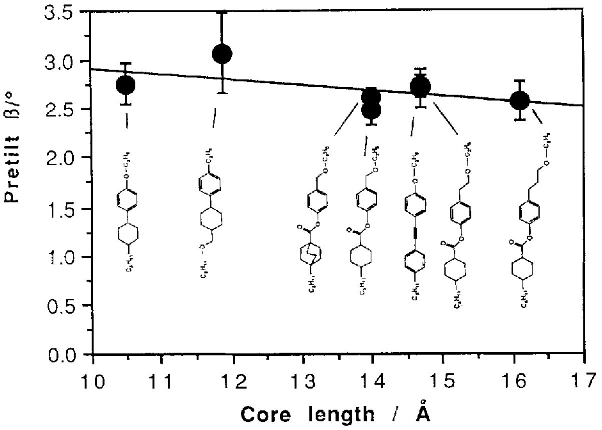


Figure 13. Pretilt angles as a function of core length for 10 mol% of several dopants in ZLI 1602.

4.5. *Three real life calculations*

As a detailed example of our calculations, and a check on the method, we will show the complete calculation of the pretilt angles for three complex commercially available mixtures. All three mixtures consist of components with fully aromatic two or three ring cores which reduces the uncertainty in the calculations of the shape of the components. In addition, all the components also have a cyano-group at one end, thus ensuring that the angle between the surface and the optical axis will be constant.

The structures of the compounds listed in tables 4, 6, 7 and 8, are shown in figure 14, together with their abbreviations. In table 6 we have given the concentration of the different components in RO-TN-403, and the shape parameter, α, of each. The average shape is a weighted average over the concentration of all the species, and is given at the bottom of column 3. For each core we have calculated the Parachor using standard atomic and bond contributions [30], and the mass. This gives us the relative Parachor in column 6. For 5CB on *s*-BPDA-6, the in-plane order was previously found to be 0·292. Of this we have found 40 per cent (0·1168) to be due to the core and 20 per cent (0·0584) to be due to each of the odd-numbered methylene groups. By scaling the value for the 5CB core with the specific Parachor, we obtain the core contributions to the in-plane order. For example, for 5-PyP we have $(2{\cdot}116/2{\cdot}299)\cdot 0{\cdot}1168 = 0{\cdot}1075$. The results for all the cores are shown in column 7. Adding the same contributions as for 5CB for the alkyl chains, we obtain the final contribution to the in-plane order in column 8. For the compounds with the alkyl chain attached directly to the core this means adding 0·0584 for each odd-numbered methylene group. For the compounds with alkoxy groups, the first methylene group (and subsequent odd-numbered methylene groups) points away from the long axis, while the even numbered methylene groups point along the long axis. For the alkoxy compounds we thus add 0·0584 for each even numbered methylene group. The contribution from the oxygen atom is already incorporated into contribution from the core. The weighted average is given at the bottom of the column.

We now have the average shape of the mixture $\alpha = 3{\cdot}44°$ and the average in-plane order $a_l = 0{\cdot}2680$. These values can be used for the calculation of the expected pretilt angle. For thick cells the pretilt is given by $\beta_{obs} = a_l(\beta_0 - \alpha)$. We have found that β_0 is 16° for the cyano-group on *s*-BPDA-6. Inserting the observed value for β_0, together with the estimates for α and a_l, we obtain $\beta_{obs} = 0{\cdot}2680{\cdot}(16° - 3{\cdot}44°) = 3{\cdot}37° \pm 0{\cdot}25°$, the error is mostly due to the experimental uncertainly in determining a_l for 5CB. The experimental result for RO-TN-403 was

Table 6. The composition (in mol %) of RO-TN-403. The abbreviations are given in figure 14. For each compound, the table lists the shape (α), the mass of the core, the Parachor of the core and the specific Parachor. From this we have calculated the contribution to the inplane order (a_1) from the core and the full molecule for each component.

Compound	Concentration/per cent	Shape/(α)/°	Mass m/a.u.	Parachor [P]	Specific Parachor [P]/M	Core a_1	Total a_1
5CB	45·7	3·9	178·2	409·7	2·299	0·1168	0·292
5OCB	23·7	3·1	194·2	429·7	2·213	0·1003	0·2171
5PyP	4·5	3·9	180·2	390·9	2·117	0·0838	0·2590
7PyP	9·4	6·1	180·2	390·9	2·117	0·0838	0·3174
T15	7·4	1·0	254·3	582·6	2·291	0·1152	0·2904
4PPyP	9·1	1·0	256·3	563·8	2·200	0·0979	0·2147
Average		3·44					0·2680

3·59° ± 0·15°. The agreement between calculations and observations is very good.

Table 7 gives the composition of RO-TN-103, together with the shape of the individual components and their relative in-plane order. Employing the same procedure as for RO-TN-403, we can also calculate the expected pretilt angle for this mixture on *s*-BPDA-6. The calculated pretilt is (16° − 3·72°)·0·2948 = 3·62° ± 0·25°. Experimentally it has been found to be 3·98° ± 0·10° [3]. Again we find good agreement between calculations and observation. The same calculations were also performed for E26M with the composition and values given in table 8. The expected pretilt is $\beta_{\rm obs} = (16° - 4{\cdot}93°){\cdot}0{\cdot}3057 = 3{\cdot}38° \pm 0{\cdot}25°$ on *s*-BPDA-6. Cells filled with this mixture gave a pretilt of 3·42° ± 0·18°. Again we have a very satisfactory agreement between theory and experiment.

When the surface angle (β_0) and the in-plane order for one component is known, we can calculate these constants for other components with the same end group, and thus estimate the pretilt for any mixture. So far our procedure has only been tested for the cyano-end group.

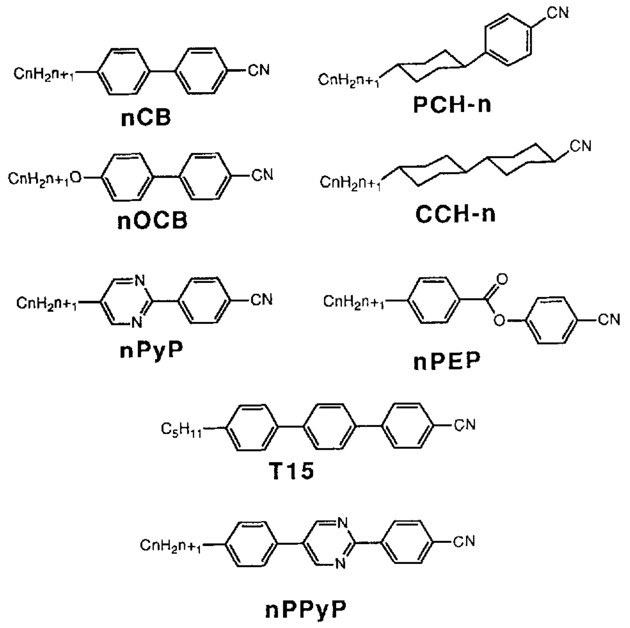


Figure 14. The structures of the compounds in tables 4, 6, 7, and 8, together with their abbreviations.

Table 7. The composition (in mol %) of RO-TN-103 together with the shape and in-plane order. The abbreviations are given in figure 14.

Compound	Percentage	Shape (α)/°	In-plane order a_1
5-PyP	11·2	3·9	0·2677
4CB	8·9	2·7	0·2336
5-PEP	9·7	3·0	0·3181
7-PyP	22·9	6·1	0·3261
6-PEP	13·4	4·1	0·3181
7-PEP	13·6	5·0	0·3765
4-PPyP	20·3	0·6	0·2198
Average		3·72	0·2948

Table 8. Composition (in mol %) of E26M together with the shape and in-plane order. The abbreviations are given in figure 14.

Compound	Percentage	Shape (α)/°	In-plane order a_1
6CB	40	5·1	0·292
1OCB	10	10·4	0·4088
12OCB	10	7·3	0·4507
3OCB	15	1·8	0·1587
8OCB	15	5·0	0·3339
T15	10	1·0	0·2904
Average		4·93	0·3057

5. Conclusions

The population distribution model for the pretilt angle can explain all the observed data for the relationship between the observed pretilt and the chemical structure of the nematic material.

The in-plane order is a function of both the substrate–mesogen interaction and the mesogen–mesogen interaction. The substrate–mesogen interaction is most important for the cyano-compounds. The interaction between mesogens, giving rise to changes in the in-plane order a_1, can be calculated by group contributions via the Parachor and the molecular mass for each species.

The total interaction and the average shapes of the mesogens in the mixture can be calculated as a weighted average of the different species in the mixture.

For mixtures with a cyano-end group, the in-plane order can be treated as a product of one contribution from the surface and one from the mixture. For the di-alkyl compounds, and in-plane order depends only weakly on the structure of the mesogen.

Mesogens also form different angles with the surface; this angle seems to be related to the strength of the Hammett constant of the polar end group, and the steric interactions with the surface.

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