Molecular Structure and Mesomorphic Properties of Thermotropic Liquid Crystals. II. Terminal Substituents

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The effect of terminal polar and nonpolar substituents on the thermodynamic stability of the mesophase is discussed. Mesomeric as well as steric effects influence the packing of the molecules and consequently the clearing point. It is necessary to consider the effect of substituents in connection with the nature of the rigid core. The influence of molecular association and conformational equilibria on the stability of the mesophase is described. Isolated electron densities lead to repulsions between neighbouring molecules, thus destabilizing the mesophase and the layered structure if present.

Introduction

The attractive interactions between liquid crystal (LC) molecules provide the background necessary to sustain the condensed state while the repulsive forces (steric effects) control the packing and determine the liquid structure. Although the orientation dependent energy is required to account for a thermotropic phase transition, the steric factors (packing) were shown to play a dominant role in determining the type and stability of the mesophase, since they govern the packing and consequently the intermolecular separation. The interaction forces influence the mesophase stability and the orientational order but strongly depend on the intermolecular separation. The effect of structural differences in the rigid core of the molecules on the mesomorphic properties was described in Part I [1].

Substitution of the terminal hydrogen atoms of a rigid anisotropic molecule by other atoms or groups is known to strongly enhance the thermodynamic stability of the mesophases [2–6]. The increased mesophase stability was attributed to intermolecular attractions resulting from the polarity and polarizability of the substituents [2–5]. Recently, it was shown that nonpolar alkyl groups also stabilize the mesophase mainly as a result of increased geometrial anisotropy [6]. In this paper the role of terminal substituents in stabilizing the mesophase or favouring a certain one will be discussed with regard to their effect on the packing of the molecules.

Experimental

The mesomorphic properties were investigated by DSC and microscopy using a PE-DSC 2 and a Leitz Orthoplan equipped with a modified Mettler FP 5/52 heating stage. The hot-stage was cooled by means of a cold nitrogen gas stream obtained from liquid nitrogen, and the transition temperatures were measured at a heating rate of 0.2 °C/min. The differential thermal analysis was carried out at a rate of 5 °C/min. Data which have been measured in this laboratory are given to 0.1 °C while those taken from the literature are given in round figures. The investigated products were either synthesized or purchased and purified to a purity of 99.7% or better as determined by GLC using a 3% OV 25 or a 3% silar 10C open tubular column. The synthesized products, except the dialkyl bicyclohexanes whose synthesis was previously described [1], are all esters which were prepared by standard methods.

Results and Discussion

The clearing points of the investigated compounds are compared to those of known similar series in Tables 1–5. In this context only experimentally measured clearing points were considered, since virtual clearing points obtained by extrapolation from mixtures were often found to divert strongly from the actual values and deviations up to 40 °C were observed in some of the systems investigated [7, 8]. In the following, an attempt is made to explain the effect of terminal substituents on the type and stability of the mesophase in relation to their influence on the packing of the molecules.

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The effect of terminal substituents on the stability of the mesophase has been mostly generalized [2–5]. However, it is necessary to consider their effect in connection with the nature of the rigid core to which they are attached. An alicyclic compound which has the same terminal substituent as an analogous aromatic derivative can assume a different configuration or conformation and consequently a different packing. Differences in packing were shown to influence the type of mesophase as well as its stability [1]. The charge distribution in the molecule can also be different, which in turn affects the packing and the intermolecular forces. These factors strongly influence the thermodynamic stability of the mesophase. The common substituents in LC's can be devided into polar (e.g. CN, NO_2) and nonpolar (e.g. alkyl, alkoxy) substituents.

Cyano Group

The cyano group is an anisotropic strong polar substituent, whose dipole moment is −3.47 D when attached to an aliphatic rest, and −4.05 D if it is conjugated with an aromatic moiety [9]. Although the major effect of dipolar groups attached to mesogenic molecules is observed in the dielectric properties, they do also influence the mesophase stability probably due to increased molecular interactions and due to the molecular association usually observed in polar compounds [10], which affect the packing of the molecules. The nematic isotropic (N–I) transition temperatures of some terminally cyano-substituted LC's are given in Table 1.

From quite a number of compounds [25], it is evident that mesogenic aromatic nitriles possess higher clearing points than the corresponding nonpolar compounds where the cyano group is replaced by a methyl group. The nitriles also show a tendency to form nematic phases while the alkyl derivatives generally tend to show smectic phases. For example 4-n-heptyl-4′-methyl biphenyl has a S–I transition at 29.4 °C, compared to a N–I transition at 42 °C for compound 2. This is probably due to the polarization of the aromatic molecule caused by the cyano group and the resulting charge distribution which leads to a head-to-tail arrangement of the molecules with opposing charges at minimal separation (molecular association). While it is probably true that the electrostatic forces resulting from this dipolar interaction are only of secondary im-

Table 1. The N–I transition temperature (°C) of different cyano substituted mesogenic compounds.

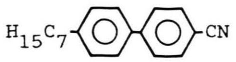
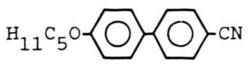
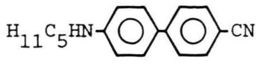
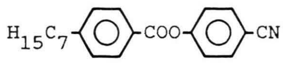
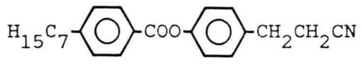
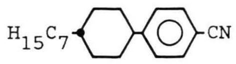
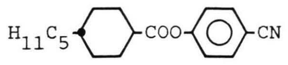
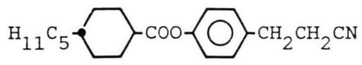
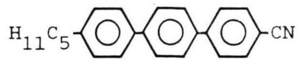
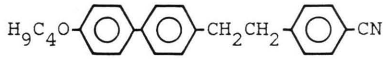
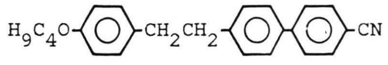
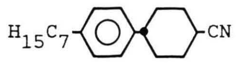
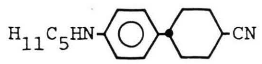
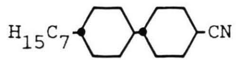
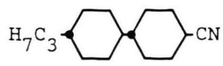
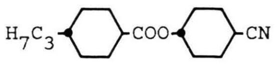
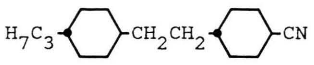
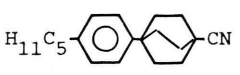
1)		51 [11]
2)		42 [12]
3)		68 [12]
4)		90.7 [13]
5)		57 [14]
6)		24 [15]
7)		58.0 [16]
8)		79 [17]
9)		51 [17]
10)		241 [18]
11)		240 [12]
12)		175 [19]
13)		166 [19]
14)		no mesophase above room temp. [16, 22]
15)		16.9 [21]
16)		83 [16]
17)		80 [16]
18)		176 [22]

Table 1 (continued).

19)		no meso- phase above room temp.
20)		48 [23]
21)		50 [24]

portance for the stabilization of the mesophase, the molecular association alters the packing of the molecules compared to that of nonpolar compounds. A polar liquid can in fact be considered as an equilibrated mixture of "monomers" and "dimers" [1], whose constitution depends on the degree of association which in turn strongly depends on the molecular structure as well as on the equilibrium conditions [10]. It is clear that such a mixture of short "monomers" and long "dimers" whose concentrations are temperature dependent can hardly form a layered structure, specially at elevated temperatures, and a nematic phase is favoured. The length of the "dimers" depend on the degree of overlapping of the rigid cores while the width remains unchanged. It is well known that the mesophases of long molecules with high geometrical anisotropy are more thermodynamically stable than those of short ones. Therefore, the molecular association enhances the clearing points of polar compounds. The rotation of the molecules has also to be integrated in this simplified picture, since the "monomers" and "dimers" rotate around their long molecular axes but probably not independently as Dunmur and Miller [26] pointed out from perpendicular correlation factor ($g_\perp$) arguments. Interruption of the conjugation between the cyano group and the aromatic rigid core decreases the charge separation and consequently the degree of association which minimizes the above described effect. In compounds 6 and 9 the cyano groups were separated from the phenyl moiety by two methylen groups to keep them parallel to the long molecular axes and prevent a change of the geometry of the molecules. In both cases the N−I transition temperatures are about 30 °C lower than that of the conjugated compounds 5 and 8. Smectic phases were also observed in these homologous series [15, 17], which is not the case in the cyano phenyl derivatives [14, 17].

The biphenyl derivative 2 has a slightly lower clearing point than the phenyl pyrimidine 1 probably due to the rotated planes of the aromatic rings as well as the absence of the nitrogen atoms in biphenyls and the consequent effects on the packing and molecular interactions. The alkoxy and alkylamino biphenyls 3 and 4 possess much higher N−I transition temperatures than the corresponding alkyl derivative [12] due to the electron donating character of these substituents and their effect on the polarizability and charge distribution in the molecules. Elongation of the flat rigid cores of 1 and 2 by another flat phenyl group (compound 10 and 11) increases the geometrical anisotropy, gives a greater separation of the charges (stronger association) and leads to stronger molecular interactions, thus stabilizing the mesophase. Interruption of the conjugated flat rigid core of compound 11 by two angular methylene groups (compounds 12 and 13) strongly lowers the clearing point due to mesomeric and geometrical reasons [1]. Although the two methylene groups increase the length of the rigid core, they do separate it into two displaced flat parts and interrupt the partial conjugation of the π-electron system. They thus, lead to N−I transition temperatures about 70 °C lower than that of compound 11 although compounds 12 and 13 possess alkoxy terminal groups which usually lead to higher clearing points. The effect of terminal cyano groups on the clearing point has to be considered in connection with the effect of all other substituents present, specially if they are also polar.

Replacement of the phenyl moiety attached to the alkyl group in the biphenyl 2 by a trans-cyclohexyl rest (compound 7) enhances the clearing point although the π-electron system is shortened and the charge separation is partially decreased. This is probably due to the fact that the staggered form of the cyclohexyl moiety is geometrically harmonious with the trans-conformation of the alkyl group, thus leading to a denser packing. However, attaching the cyano group to a cyclohexyl ring leads to a drastic decrease in the thermodynamic stability of the mesophase as can be seen in compounds 14, 15, 18 and 19. Both compounds 15 and 18 show N−I transitions which are about 70 °C lower than those

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[1] The terms "monomers" and "dimers" are used here for simplicity reasons. What is ment is the existance of a short range anti-parallel correlation.

of the corresponding aromatic derivatives 4 and 10, while compounds 14 and 19 did not show any mesophase. This can be attributed to two factors a) low degree of association in these compounds due to decreased charge separation, b) low conformational free energy difference ($-\Delta G^\circ$) between the cyano cyclohexyl ee and aa conformers, and the isotropic character of the aa conformer [21]. Both $-\Delta G^\circ$ values of the substituents in 1- and 4-positions of a cyclohexyl moiety are of importance for the conformational equilibrium, since these values are additive. This is illustrated by the relatively high clearing point of compound 20 where the 1-position of the 4-cyano cyclohexyl moiety is occupied by a methylene group instead of the oxygen atom of the carboxyl group in compound 19. The cyano bicyclohexyl derivative 16 shows a much higher clearing point than those of both phenyl cyclohexanes 7 and 14 although the $-\Delta G^\circ$ value of the phenyl group is similar to that of a cyclohexyl rest. A possible explanation for this result is that the above argument (b) is probably not valid in this case. For geometrical reasons, the bicyclohexanes possess quite a dense packing which leads to high clearing points even in the dialkyl derivatives [1] which usually have low clearing points (e.g. aromatic mesogens). This dense packing and the existence of smectic phases in these compounds will probably lead to unusual $-\Delta G^\circ$ values when measured in the liquid crystalline state. Compound 17 for example, possesses almost the same clearing point as the trans,trans-4,4′-di-n-propyl bicyclohexane (S−I 81.8 °C), although the propyl group usually has a higher $-\Delta G^\circ$ than the cyano substituent. The $-\Delta G^\circ$ values of the different substituents reported in the literature [27] were measured in isotropic solutions, and the absolute values could be different in the ordered mesophases due to stronger molecular interactions and denser packing. However, the relative $-\Delta G^\circ$ values are probably applicable to LC's as long as similar molecules (similar packing) are compared to each other within the same mesophase.

If the above arguments are correct, it should be expected that attaching the cyano group to a nonflexible alicyclic ring will lead to LC's with higher clearing points than those of compounds 14 and 15. This is actually the case in the cyano bicyclooctane derivative 19 which has a similar N−I transition to that of a biphenyl or a phenyl pyrimidine derivative but much higher than that of compound 14 or 15.

Alkyl Group

A terminal n-alkyl group increases the number of σ-bonds in the molecule and consequently the intermolecular attractive forces as well as the geometrical anisotropy. This usually enhances the thermodynamic stability of the mesophase. However, the effect strongly depends on the conformation assumed by the alkyl chain because of its influence on the intermolecular separation. In the isotropic phase an alkyl chain can assume different trans-(anti) and gauche-conformations [28], but the aligned environment in a LC (rigid cores) is expected to somewhat restrict the conformational freedom of the alkyl chains[2]. In other words, the long range order of the rigid parts of the molecules introduces a certain finite chain order [29, 30]. However, it must also be expected that the flexible alkyl chains will affect the orientational order of the rigid parts [31]. It is well known that in the isotropic phase the energetically favoured anti(a)-conformer of n-butane is in equilibrium with the gauche(g)-conformer. The ag-conformer of n-pentane as well as the aag- together with the aga-conformer of n-hexane constitute about 50% of the conformation equilibrium mixture of both compounds at 300 K [32].

The influence of the alkyl chain length on the clearing temperature has been the subject of extensive studies [2, 5, 33, 34], and is shown in Tables 2−4. In homologous series of nematogens with alkyl chains longer than propyl, a regular alternation of the N−I transition temperature is observed with higher values for the homologues whose alkyl chains contain an odd number of carbon atoms. The amplitude of alternation usually decreases with increasing chain length. Beside the alternation, there is usually either a general increase (ascending series) or decrease (descending series) of the clearing points in certain series, while in others it remains more or less steady (steady series) as can be seen from Tables 2−4. In general, there is an increase of clearing point with increasing chain length in series with low N−I transitions, while those with high clearing points either remain steady or suffer a decrease in their N−I transition on going to the higher homologues. These phenomena have been related to changes in the anisotropy of polar-

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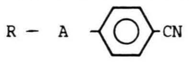
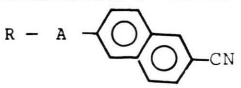
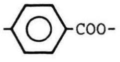
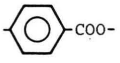
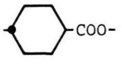
[2] Flexible solute dissolved in a solvent consisting of hard rods.

Table 2. The effect of alkyl chain length on the N–I transition temperature (°C) of cyano-substituted LC's.





A R							
CH_3	50.7	−35.0	63.3	214 [22]	186 [16]	174 [35]	119 [35b]
C_2H_5	21.5	1.9	60 [14]	225 [22]			144 [35b]
C_3H_7	30.6	46 [16]	51 [14]	244 [22]	230 [16]	160 [35a]	173 [35b]
C_4H_9	17 [12]	41 [16]	42.5	234 [22]		142 [35a]	167 [35b]
C_5H_{11}	35 [12]	55 [16]	56.8	231 [22]	219 [16]	154 [35a]	169 [35b]
C_6H_{13}	29.3	47 [16]	47.6	225 [22]	210 [16]	138 [35a]	161 [35b]
C_7H_{15}	42 [12]	58.0	57 [14]	219 [22]	206 [16]	135 [35a]	161 [35b]

izability with increasing chain length. Different attempts, based on the Maier-Saupe theory have been made to calculate the clearing points of the members of homologous series. De Jeu [33] suggested to include a packing entropy term in these calculations. Divergence from the above described behaviour was observed when virtual transitions of the lower homologues ($< C_3$) were considered [34]. At the first sight, this was thought to be due to erroneous N–I values obtained by the extrapolation method. The experimentally observed values for many short LC's however, show the same divergence (Tables 2–4).

The introduction of a methyl group in a terminal position of a flexible alicyclic moiety (e.g. cyclohexane) was found to enhance the thermodynamic stability of the mesophase much more than if it is introduced in a rigid aromatic rest (e.g. phenyl) [6]. This was attributed to the relatively high $-\Delta G^\circ$ of an alkyl group, and the consequent effect on the conformational equilibrium of the cyclohexyl moiety. From Tables 2–4 it can be seen that the N–I transition increases on going from the methyl to the ethyl derivative if the alkyl group is attached to a staggered part of the rigid core (e.g. cyclohexyl) and decreases if attached to a flat part (e.g. phenyl). The n-propyl cyclohexyl derivatives show a dramatic increase in clearing point compared to the methyl and ethyl derivatives while the n-propyl phenyl homologues possess lower or almost the same clearing temperature as the preceding odd homologue (methyl). If the flat rigid core to which the propyl group is attached consists of two directly linked aromatic units, then the drop in clearing point is much greater than if the two units were separated by a staggered linkage. Elongation of the alkyl chain attached to a staggered cyclohexyl moiety leads to a geometrically harmonious unit, since the stretched propyl group is also staircase like, and the clearing point is enhanced. The above described behaviour of the short members of homologous series is irrespective of the behaviour of the higher homologues i.e. irrespective of whether the series is descending or ascending. These results show that the packing effects (steric) strongly influence the thermodynamic stability of the mesophase and have to be considered when the effect of chain length on the clearing point is discussed. This is in accordance with the packing effects observed in molecules with different rigid cores [1, 6–8, 21]. Higher homologues ($> C_3$) have more possibilities for gauche- and anti-conformations, but some of these conformers are energetically favoured depending on the temperature and structure of the rigid core. At high temperatures the alkyl chains possess a higher degree of rotational and conformational freedom. However, this movement is restricted by the densly packed rigid cores, and the restriction is expected to be greater when the geometrical anisotropy of the molecule is increased i.e. longer rigid core. The thermodynamically favoured a-conformation of the alkyl chain is also expected to give a denser packing with a staircase like rigid core (cyclohexane) rather than with a flat aromatic one, and a further restriction on the rotational movement of the alkyl chains can be expected. Therefore it is not only the clearing

Table 3. The effect of alkyl chain length on the clearing point (°C) of *n*-alkyl substituted LC's.

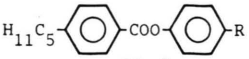
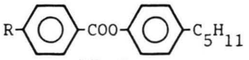
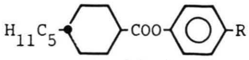
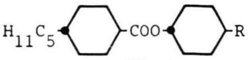
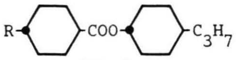
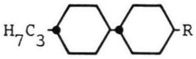
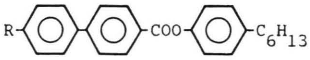
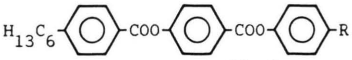
R=	CH_3	C_2H_5	C_3H_7	C_4H_9	C_5H_{11}	C_6H_{13}	C_7H_{15}
 N–I	15.6		19.5		26.0		28.6
 N–I	13.6		18.6		26.0		29.6
 N–I	45 [17]	29 [17]	43.6		48 [17]		
 N–I	8.3	21.0	52.1		72 [17] (S–I)		
 N–I	–18.2	5.5	36.6	38.0	52.1		
 S–I	25.7		81.8				
	194 [36]		165 [36]		163 [36]		162 [36]
	188 [36]	174 [36]	178 [36]	174 [36]	175 [36]	163 [36]	171 [36]
 N–I	183 [16]	171 [16]	174 [16]	169 [16]	172 [16]		
 N–I	123 [37]		154 [16]	174 [16]	156 [16]		
 N–I	155.9		183 [16]				
 N–I	182 [38]		176 [38]	168 [38]			

Table 4. The effect of alkyl chain length on the N–I transition temperature (°C) of *n*-alkoxy substituted LC's.

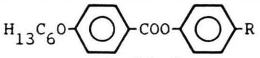
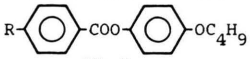
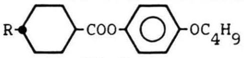
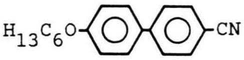
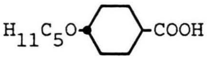
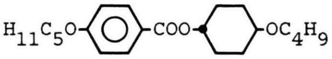
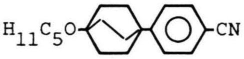
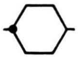
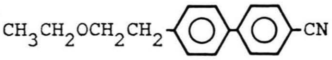
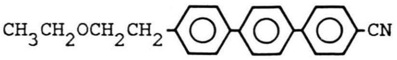
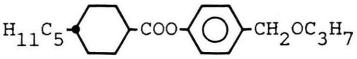
R	 N–I	 N–I	 N–I
CH_3	52 [25]	52 [25]	27 [17]
C_2H_5	45 [25]	45 [25]	43 [17]
C_3H_7	59 [25]	59 [25]	73 [17]
C_4H_9	53 [25]	46 [25]	69 [17]
C_5H_{11}	63 [25]	58 [25]	81 [17]
C_6H_{13}	59 [25]	49 [25]	76 [17]
C_7H_{15}	64 [25]	57 [25]	81 [17]

Table 5. The effect of terminal *n*-alkoxy groups on the N–I transition temperature (°C) of mesogenic compounds.

22)		77 [12]
2)	$H_{15}C_7-$	42 [12]
23)		no mesophase [17] above room temp.
24)	$H_{13}C_6-$	97 [17]
25)		no mesophase [17] above room temp.
26)	$-C_4H_9$	41 [17]
27)		no mesophase [43] above room temp.
28)	$H_{13}C_6-$	86 [12]
29)		241 [44]
30)		223 [44]
31)		157 [44]
32)		no mesophase [45] (Fp 49 °C)
33)	$H_{11}C_5-$	35 [12]
34)		215 [45]
11)	$H_{11}C_5-$	240 [12]
35)		5 [46]
36)	$-CH_2CH_2CH_2OCH_3$	32 [46]
37)	$-C_5H_{11}$	48 [17]

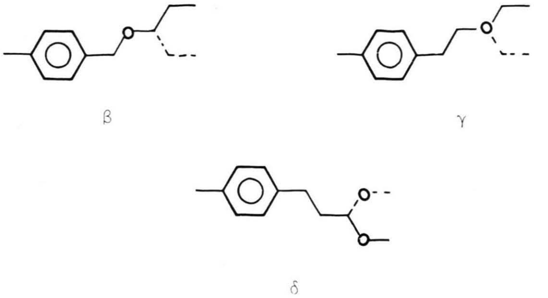


Fig. 1. Structure of alkoxy alkylene substituted compounds.

temperature which determines whether the series is ascending or descending, but also the geometry of the molecule as can be seen from the data given in Tables 2–4.

Alkoxy Group

The alkoxy group is one of the substituents which have been commonly used in LC's, since the C–O bond angle (111°) is almost the same as that of the C–C bond (112°). However, if the oxygen atom is directly attached to an aromatic moiety then its free electrons get conjugated to the π-electron system, which icreases the molecular interactions and consequently the thermodynamic stability of the mesophase. The polarization of the π-electron system may also lead to molecular association whose degree depends on the other substituents attached to the aromatic system. The effect of molecular association on the clearing point has already been discussed before (cyano group). The influence of an alkoxy group on the clearing point of an aromatic mesogen can easily be seen from a comparison between compounds 2 and 22 (Table 5). The length of the alkyl chain in the alkoxy group has the same effect described above (alkyl group), with the exception that the O-atom has to be counted as a member of the chain [2, 5].

In alicyclic compounds the electron pairs of the oxygen atom are not conjugated and the isolated electron density leads to repulsion between neighbouring molecules, thus increasing the intermolecular separation. As a result, the thermodynamic stability of the mesophase is decreased, which is the case in compounds 23, 25 and 27. In cyclohexyl derivatives, the small $-\Delta G°$ of an alkoxy group shifts the conformational equilibrium, and the concentration of the isotropic aa-conformer is increased, thus leading to a further destabilization of the mesophase [21]. Dewar and Goldberg [44] showed that replacing a phenyl group in compound 29 by the rigid aliphatic bicyclooctane moiety (compound 30) lowers the clearing point by 18 °C only, while a flexible cyclohexane ring (linked to two oxygen atoms, compound 31) lowers the N–I transition by 84 °C. This clearly demonstrates the above described effects.

Incorporation of the oxygen atom within the alkyl chain, i.e. replacement of one of the C-atoms by oxygen, leads also to repulsion between neighbouring molecules. The resultant intermolecular separation, which influences the thermodynamic stability of the mesophase, depends on the position of the oxygen atom in the alkyl chain (Figure 1). The δ-position has the smallest destabilizing effect as can be seen from compounds 32–37. Although the destabilization of the mesophase is undesired, these repulsion forces can be a powerful tool to favour the nematic phase, since they hinder a layered structure as can be seen in many compounds described in reference [46]. However, the O-atom has to be situated in such a position that the repulsion forces hinder the formation of a smectic phase but do not completely destabilize the mesophase. The same effects were observed when a methylenoxy group was used as a part of the rigid core, as in the cyclohexyl cyclohexylmethyl ethers [1, 47].

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