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Invited Article

The effect of the position and configuration of carbon–carbon double bonds on the mesomorphism of thermotropic, non-amphiphilic liquid crystals

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The influence on their mesomorphic behaviour of introducing a carbon–carbon double bond into the chain, central linkage and alicyclic rings in the core of nematic and smectic liquid crystals (LCs) is discussed. Mesogens incorporating a *trans*-carbon–carbon double bond conjugated with an aromatic ring exhibit high mesophase–isotropic transition temperatures (T_c). However, they are photo-sensitive and can convert to the non-linear, non-mesogenic *cis*-isomers under the action of light. Non-conjugated double bonds in the terminal chain of mesogens can also lead to higher nematic and smectic C transition temperatures than those of the corresponding materials without a double bond, although the effect is not nearly as great. The position and *trans-cis*-configuration (E/Z) of the double bond are seen to be decisive. The combination of a hetero-atom (dipole effect) and the added rigidity imposed by the carbon–carbon double bond (steric effect) with a *trans*-configuration (E) in the terminal alkyl chain attached to the core of a liquid crystal molecule can give rise to a broad nematic phase. The double bond in the terminal chain of nematogens advantageously modifies the elastic constant ratios, as well as other properties of relevance to LCDs, especially for supertwisted TN-LCDs. The double bond in a central linkage gives rise to a broad spectrum of effects, sometimes suppressing undesired smectic phases and widening the nematic phase temperature range. Non-conjugated double bonds in the molecular core in the form of cyclohexene rings generally lead to lower transition temperatures, although smectic phases are sometimes suppressed and a nematic phase is observed. A conjugated double bond in a cyclohexene ring gives rise to a slightly higher T_{NI}. The effect on the transition temperatures of the double bond in steroid systems is complex.

1. Introduction

Systematic studies investigating the influence of the configuration and position of carbon–carbon double bonds on the liquid crystal transition temperatures of model systems incorporating various rings and heteroatoms in the core and the chains may help to elucidate the relative merits of the Maier–Saupe theory [1], the various Hard Rod theories [2] and Combined theories [3–6] for the nematic mesophase. The preparation of liquid crystal materials with carbon–carbon double bonds of a defined configuration in the terminal chain, central linkage or in alicyclic rings in the core of the molecules allows the effect of known changes in the geometry and shape of individual molecules to be correlated with differences in the transition temperatures for the bulk material. The combination of double bonds and heteroatoms, especially oxygen atoms, allows polar and steric effects to be varied systematically and their effects on the liquid crystal transition temperatures to be studied. A better understanding of the property/structure relationships of liquid crystals would facilitate the design and synthesis of optimized mesogens for electro-optic liquid crystal display devices (LCDs). This has already been shown to be of direct commercial and technological relevance for LCDs based on passively or actively addressed twisted nematic (e.g. TN [7], TFT [8], MIM [9], etc.), or super-twisted configurations (e.g. SBE [10], STN [11], OMI [12], DSTN [13], BW STN [14], etc.), sometimes with dichroic dyes (e.g. GH [15], GHSTN [16], etc. [17]). This has also led to the development of commercial chiral smectic C (S_c^*) mixtures with improved physical properties for electro-optic display devices based on ferroelectric effects such as the surface stabilized (SSFLCDs [18, 19]), short pitch bistable (SBFLCDs [20]) and distorted helix (DHFLCDs [21, 22]) ferroelectric liquid crystal displays (FLCDs).

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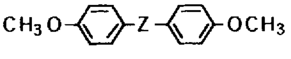
There are many known liquid crystals with a carbon–carbon double bond as part of a central linkage between two aromatic rings, such as stilbenes [23], cinnamates [24], cinnamylidene–anilines [25], etc. [26–28], see table 1. The majority of these mesogens with a *trans*- (i.e. *E*) double bond generally exhibit a nematic mesophase at high temperatures [23–28]. This was attributed to the rigidity, linearity and polarizability due to the sp^2 bonding between the two carbon atoms of the double bond, giving rise to a high length/breadth ratio and high molecular polarizability [27, 28]. However, the propensity of conjugated carbon–carbon doubles bonds to isomerize from the *trans*- to the *cis*- (i.e. *Z*) isomers under the influence of light to form non-linear, non-mesogenic systems [28] limits their use in commercial mixtures for LCDs. Attempts to stabilize the double bond by the incorporation of bulky substituents at the linkage were only partially successful [24, 26–28], see table 1. The viscosity (γ) of such materials is high and the nematic–isotropic transition temperature (T_{NI}) low compared to the parent, non-substituted stilbenes [26–28]. This can be attributed to rotation of the phenyl rings out of the plane and the consequent reduction in the degree of conjugation and molecular planarity [23].

The high T_{NI} and the photochemical and thermal instability are also found when the double bond is conjugated with only one, instead of two, aromatic rings, e.g. when it is situated between the terminal chain of a mesogen and an aromatic (e.g. phenyl, pyridinyl, etc.) ring in the molecular core, see table 2 [29, 30]. The T_{NI} is highest for the ethenes (**8** and **11**) independent of the polar nature of the end group (CH_3 or CN) attached to the double bond. Although this can be clearly ascribed, as above, to the higher degree of molecular polarizability and rigidity associated with the double bond with respect to the ethanes (**7** and **10**), which exhibit a very low T_{NI}, the lower T_{NI} for the ethynes (**9** and **12**), which should induce a smaller molecular rotation volume or at least a higher molecular polarizability, shows that the situation is not this simple and that other parameters may well be involved. The related cinnamates ($-CH{=}CHCO_2C_nH_{2n+1}$) of intermediate dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) exhibit a similar mesomorphism with a range of smectic and nematic phases at high

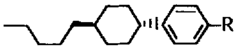
Table 1. Transition temperatures for the compounds (**1–6**).

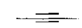
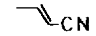
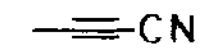


Compound	Z	Cr–N/I/°C	N–I/°C	$\Delta T_{N\text{-}I}$/°C	Reference
1	$-CH{=}C(CH_3)-$	122	98[a]	–	[24, 26–28]
2	$-CH{=}CHCOO-$	118	137	19	[24, 26–28]
3	$-SOCCH{=}CHCOS-$	176	143[a]		[25–28]
4	$-OOCCH{=}CHCOO-$	177	151[a]		[26–28]
5	$-(CH{=}CH)_2CO(CH{=}CH)_2-$	168	183	15	[26–28]
6	$-CH{=}CH{=}CH{=}N-$	168	188	20	[26–28]

[a] Represents a monotropic transition temperature.

Table 2. Transition temperatures for the 1-substituted-4-(*trans*-4-pentylcyclohexyl) benzenes (**7–12**).



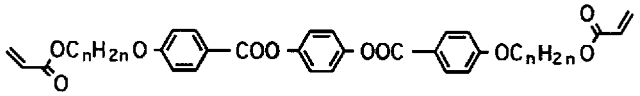
Compound	R	Cr–N/I/°C	S–I/°C	N–I/°C	$\Delta T_{N\text{-}I}$/°C	Reference
7		−9	–	−12[a]		[29]
8		27	–	92	65	[29, 30]
9		42		65	23	[29]
10		44	28[a]	–	–	[29]
11		41	–	149	108	[29]
12		50	–	129	79	[29]

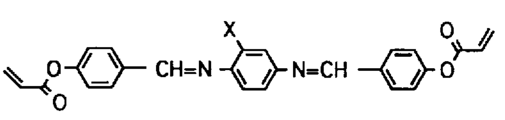
[a] Represents a monotropic transition temperature.

temperatures [27, 28]. Thus, the degree of conjugation, molecular shape and rigidity, as well as the degree of polarizability (α) are seen to be more important than $\Delta\varepsilon$ in determining T_{NI}. Cinnamates have been used to help elucidate the structures of various smectic mesophases including the chiral smectic C phase, whose ferroelectricity was first found for cinnamates [31]. However useful as research materials, they were soon found to be too unstable for mixture development for prototype FLCDs.

The effect of two adjacent *trans*-double bonds on transition temperatures is well illustrated by considering the alka-2, 4-dienoic acids (**13–16**) [32], see table 3. Hydrogen bonding between the two hydroxyl groups of two neighbouring acid molecules simulates one ring, while the *trans*-double bonds in a diene configuration can impose a semi-rigid half-ring structure on the rest of the chains. This results in a very conformationally mobile, *quasi* three-ring structure. There is still a high degree of flexibility and the possibility of free rotation about carbon–carbon single bonds. Indeed, quantum mechanical calculations indicate that the all *trans*-conformation may well not be the most thermodynamically stable conformation. A combination of these factors mitigates against the effects of the pseudo three-ring core of the dimers and leads to what would be a very low T_{NI} for three-ring structures. The stability of these unsaturated acids is insufficient for commercial applications. The corresponding saturated alkanoic acids are non-mesomorphic due to the large number of non-linear conformations that the saturated alkyl chain can adopt [27, 28].

In order to produce stable liquid crystals incorporating carbon–carbon double bonds it was necessary to reduce substantially, or eliminate entirely, the degree of conjugation between the double bond and aromatic rings in the molecular core. Non-conjugated carbon–carbon double bonds absorb light at shorter wavelengths than conjugated double bonds [28]. Therefore, they are photo- and thermally stable under the conditions specified for LCD applications. Important exceptions are mono- and di-acrylates, methacrylates and vinyl ethers attached to long aliphatic chains (i.e. spacers) [33, 34]. In this case the terminal double bond without additional substituents is activated by the adjacent carboxy (ester) group or oxygen (ether) atom. They are capable of being polymerized, sometimes spontaneously, under the influence of light, heat or catalyst and are the precursors for many side group liquid crystal polymers and anisotropic networks [33, 34]. This is even more the case for the analogous aromatic acrylates and diacrylates used to prepare the first liquid crystalline anisotropic networks from nematic, smectic and chiral nematic (N*) monomers [35–39].



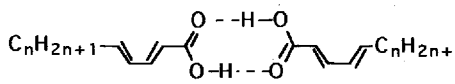


2. Carbon–carbon double bonds in the terminal chain

2.1. *trans-4-Alkenylcylohexyl-substituted compounds*

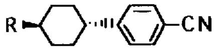
The effect of introducing a carbon–carbon double bond (C=C) in a defined position and configuration into the terminal chain of a model liquid crystal 4-(*trans*-4-pentylcyclohexyl)benzonitrile (**17**) [40] on the transition temperatures is shown in table 4 for the compounds (**18–24**) [41–43]. Steric effects due to different configurations and therefore conformations of the terminal chain were cited as the prime reason for the very large differences in the observed transition temperatures for isomers with the double bond in the same position, but with a different configuration (*E* or *Z*) [41–43]. A cylindrical shape for the molecule was assumed with an alternating *trans-cis*-conformation of the terminal alkenyl chain. These results were shown to agree qualitatively with the results obtained from molecular modelling, not of single compounds, but of ensembles of molecules [43]. This is also consistent with the higher birefringence

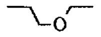
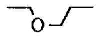
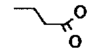
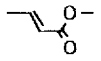
Table 3. Transition temperatures for the alka-2,4-dienoic acids (**13–16**).



Compound	n	Cr–N/I/°C	N–I/°C	ΔT_{N-I}/°C	Reference
13	1	44	46	2	[32]
14	3	23	54	31	[32]
15	4	49	70	21	[32]
16	5	32	63	31	[32]

Table 4. Transition temperatures for the 4-(*trans*-4-substituted cyclohexyl)benzonitriles (**17**–**33**).



Compound	R	Cr–N/I/°C	N–I/°C	$\Delta T_{N\text{-}I}$/°C	Reference
17		30	55	25	[40]
18	(*E*) 	16	59	43	[41]
19	(*Z*) 	–	-144^b	–	[41]
20	(*E*) 	16	-67^b	–	[41]
21	(*Z*) 	−8	54^b	–	[41]
22	(*E*) 	60	74	14	[41]
23	(*Z*) 	33	-14^a	–	[41]
24		30	10^a	–	[41]
25	(*E*, *E*) 	74	147	73	[44]
26		60	–	–	[46, 51]
27		23	–	–	[46, 51]
28		42	–	–	[46, 51]
29		52	55	3	[46, 51]
30	(*E*) 	84	–	–	[51]
31	(*E*) 	66	59^a	–	[51]
32		56	–	–	[54]
33	(*E*) 	128	119^a	–	[54]

^{a} Represents a monotropic transition temperature.
^{b} Represents a virtual (extrapolated) transition temperature.

Δn (<30%) and higher T_{NI} observed for alkenyl compounds compared to values found for the corresponding materials without a double bond in the chain. The effects of conjugation and additional molecular rigidity are illustrated by comparing the very high T_{NI} of the diene (**25**) [44] with the more modest values for the alkenyl-substituted benzonitriles (**18** and **22**) [41].

The elastic constants (k_{33}, k_{22} and k_{11}; splay, twist and bend, respectively) and dielectric constants ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) also differ greatly (a factor of 2) depending on the position and configuration of the double bond. This is of direct commercial and technological relevance for TN- and STN-LCDs. These display types require nematic liquid crystals of positive dielectric anisotropy ($\Delta\varepsilon > 0$). As the threshold voltage (V_{10}) for a TN-LCD is given [42, 43] by

$$V_{10} \propto \left(\frac{\kappa}{\Delta\varepsilon}\right)^{1/2}$$

it is clear that the dielectric anisotropy should be as great as possible for a low threshold voltage as most LCDs are battery powered. However, the threshold voltage is also dependent on the elastic constants *via* the elastic expression [42, 43]

$$\kappa = k_{11} + (k_{33} - 2k_{22})/4$$

and κ should also be as low as possible. The response times, defined as switch-on, t_{on} and switch-off, t_{off} times, should be as short as possible. Apart from the rotational viscosity γ_1, t_{off} is also strongly affected by the elastic expression κ. A low viscoelastic ratio γ_1/κ leads to short t_{off} times [42, 43].

$$t_{off} \propto \frac{\gamma_1}{\kappa}$$

The high elastic constant ratios k_{33}/k_{11} and low κ values of many alkenyl-substituted compounds give rise to very steep contrast curves and fast response times especially for STN-LCDs [42, 43]. A plethora of alkenyl-substituted cyclohexyl compounds for LCDs based on nematic materials has been prepared and consistently similar trends in the transition temperatures found. These are to be found in many commercial nematic mixtures for a variety of LCD types.

Similar trends were also found for the transition temperatures of smectic compounds on the introduction of a *trans*-double bond into a terminal chain attached to the *trans*-1,4-disubstituted cyclohexane ring, for example, see the data for the esters (**34**–**38**) in table 5. However, whereas the double bond has the tendency to suppress the smectic B (S_B) phase of nematogens, the smectic C transition temperature (T_{S_C}) is increased modestly [45]. There is no discernible difference in γ of the smectic C phase corrected for a slightly larger tilt angle, θ [45]. θ is an important parameter, as the response time, τ, is defined by

$$\tau = \frac{\lambda_{eff}}{P_s E}$$

and the relation between γ_{eff} and θ is given by

$$\gamma_{eff} = \gamma_0 \sin^2 \theta$$

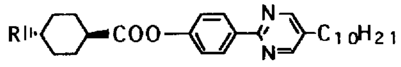
However, the presence of the double bond can lead to the disappearance of ordered smectic phases and to a broader smectic C phase than that observed for the corresponding compound without a double bond in the chain. Thus, fortuitously, the temperature range of the smectic C phase can be increased. This is of relevance to electro-optic display devices (FLCDs) based on the ferroelectric properties of the chiral smectic C phase [17–22].

2.2. (*E*)-[*trans*-4-Cyclohexyl-substituted]allyl ethers

The effect of the combination of a carbon–carbon double bond and a dipole moment associated with an oxygen atom is revealed by considering the thermal data recorded in table 4 for the ethers (**26**–**29**) [46, 51]. Only the methoxypropyl-substituted benzonitrile (**29**) with an oxygen atom at some distance from the core and without a double bond in the chain exhibits an enantiotropic nematic phase [46, 51]. However, as T_m is higher than that of the unsubstituted benzonitrile (**17**), the nematic range is narrower. The other ethers (**26**–**28**) do not exhibit an observable nematic phase [46, 51]. The smaller angle made by the carbon–oxygen–carbon bond (CH_2OCH_2) than that ($CH_2CH_2CH_2$) with a methylene unit instead of the oxygen atom may be responsible for these differences, as a greater non-linear shape is induced. The differences may also be a consequence of the enhanced flexibility of the alkoxyalkyl chain due to the lower steric hindrance of rotation about the carbon–oxygen bond compared to the carbon–carbon bond. They may also be the result of repulsive interactions due to the isolated dipole associated with the non-conjugated oxygen atom or a combination of some or all of these factors. This effect on the transition temperatures has been found for a variety of mesogens incorporating an alicyclic ring and a non-conjugated atom with a lone electron pair (e.g. nitrogen or oxygen) [25, 47–50].

At one time, organic chemists believed that in cases in which alicyclic rings lead to lower T_{NI} values than those of the corresponding aromatic compounds with a phenyl ring instead of the alicyclic ring, this could be attributed to a lower molecular polarizability and this seemed to be in agreement with the Maier–Saupe theory [1] and the general belief at the time that an aromatic molecular core strongly supported mesomorphism in non-amphiphilic compounds. This was despite a growing number of exceptions, some already referred to earlier in this article. It has since been demonstrated unequivocally by physical chemists, mathematicians and physicists that this theory is an oversimplification and that the anisotropy of polarizability is only a minor factor in determining absolute transition temperatures and the tendency for nematic mesophase formation. This is also

Table 5. Transition temperatures for the 4-(5-decylpyrimidin-2-yl)phenyl *trans*-4-alkenylcyclohexyl-1-carboxylates (**34**–**38**).



Compound	R	Cr–S/ °C	S_5–S_4/ °C	S_4–S_3/ °C	S_3–S_C/ °C	S_B–S_C/ °C	S_C–N/ °C	N–I/ °C	Reference
34		40	–	–	–	82	99	160	[45]
35		71	–	–	–	–	92	162	[45]
36		64	–	–	–	85	104	161	[45]
37		71	–	–	–	–	97	150	[45]
38		52	56	64	69	–	92	170	[45]

illustrated qualitatively by many of the results in this article. It is now evident that the length/breadth ratio and isotropic attractive forces, such as molecular polarizability, dipolar forces, etc., are primarily responsible for mesomorphic behaviour. It has been postulated that the lower T_{NI} of the ethers (**26**–**28**) was the consequence of a non-conjugated, isolated dipole [49, 50]. The difficulty in estimating the contribution of these competing effects on the mesogenic tendencies of compounds is illustrated by combining two functional groups exerting a combination of polar and steric effects in different positions of the constitutional isomers (**30** and **31**). For one ether (**30**) [46, 51] no mesomorphic behaviour could be determined, although this may be due to the high T_{m} masking a monotropic phase at a relatively low temperature. However, a monotropic nematic phase for the second ether (**31**) [51] could be observed at a temperature higher than that of the reference substance (**17**) [40].

The effect on the transition temperatures of introducing an oxygen atom and/or a double bond into the pentyl side chain of a model apolar (alkyl/alkoxy) compound to produce the 3-methoxypropyl-, (*E*)-pent-1-enyl- and 3-methoxy-(*E*)-propenyl-substituted compounds (**39**–**42**) is illustrated by the data collated in table 6 [51, 52]. Similar results for T_{NI}, but not for T_{m}, to those for the polar analogues (see table 4) are observed. The incorporation of an oxygen atom into the ether (**39**) to produce the 3-methoxypropyl-substituted ether (**40**) results in a much lower T_{m} and a lower T_{NI}. However, as T_{m} is decreased much more than T_{NI}, a relatively broad nematic phase, just above room temperature, is observed. The incorporation of a carbon–carbon double bond instead of an oxygen atom into the ether (**39**) [55] to produce the 1-pentenyl-substituted ether (**41**) results in a lower T_{m}, but a higher T_{NI}. The result is also a relatively broad nematic phase, but at higher temperatures. The introduction of an oxygen atom *and* a carbon–carbon double bond into the ether (**39**) to produce the allyl ether (**42**) leads to a nematic phase with the widest temperature range just above room temperature. The results in this table serve to illustrate once again the point that the thermal range of a mesophase is also dependent on T_{m} as well as on the T_{NI} or temperature of transition to another phase. This must also be taken into account in the design of new mesogens, although the effect of molecular changes on T_{m} is much more difficult to predict.

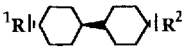
The effect of the 3-methoxy-(*E*)-propenyl-side chain on smectic phases is revealed by consideration of the thermal data in table 7 [52]. The ether (**43**) only exhibits a smectic B phase, while the intermediate alkyl/alkenyl derivative (**44**) exhibits both a smectic B and a nematic mesophase at elevated temperatures. However, the nematic phase for the compound (**45**), containing a second double bond and an oxygen atom, is much wider than that of the ether (**44**). This is due to the absence of a smectic phase above room temperature, although the T_{NI} of both compounds are comparable. Only other

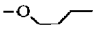
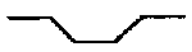
Table 6. The transition temperatures for the *trans*-1-(4-ethoxyphenyl)-4-substituted cyclohexanes (**39**–**42**).

Compound	R	Cr–N/I/°C	N–I/°C	$\Delta T_{\mathrm{N\text{-}I}}$/°C	Reference
39		52	47[a]	–	[55]
40		18	38	20	[52]
41		32	55	23	[52]
42		19	46	27	[52]

[a] Represents a monotropic transition temperature.

Table 7. Transition temperatures for the bicyclohexyl compounds (**43**–**45**).



Compound	R^1	R^2	Cr–S_B/N/°C	S_B–N/I/°C	N–I/°C	$\Delta T_{\mathrm{N\text{-}I}}$/°C	Reference
43			25	85	–	–	[52]
44			38	73	95	22	[52]
45			10	–	92	82	[52]

methyl (*E*)-allyl ethers (**46–49**) with a short alkenyl chain, with the second double bond in a position and with a configuration (*E*) known to promote nematic behaviour, possess a broad nematic phase with a high T_{NI}, see table 8. Longer alkenyl chains induce the smectic B phase typical for bicyclohexyl compounds of this kind. As the presence of a smectic B phase defines the lower temperature limit of commercial mixtures for LCDs, it is vital that the smectic B transition temperatures are as low as possible.

Although the analogous polar two-ring methyl (*E*)-allyl ethers (e.g. with a terminal cyano or halogeno group instead of an alkyl or alkoxy chain) often exhibit a low T_m, they are not generally mesomorphic (an exception is compound (**31**) in table 4, where a monotropic nematic phase is observed). The corresponding polar three-ring methyl (*E*)-allyl ethers exhibit higher T_m, but also high T_{NI}. This leads to broad nematic phases often due to the strong suppression of smectic phases observed for related compounds. These results for polar methoxy (*E*)-allyl ethers and the thermal data for the analogous apolar ethers tabulated in tables 6–8 suggest that synergetic effects due to the presence of both an oxygen atom and a carbon–carbon double bond can lead to wide nematic temperature ranges. These methyl (*E*)-allyl ethers are easy to synthesize as pure *trans*-isomers, as, no isomerization of the carbon–carbon double bond is necessary, as the *trans*-isomer is by far the predominant product of the Wittig–Horner reaction used to create the double bond. Traces of the undesired *cis*-isomer are removed by recrystallization.

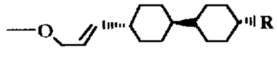
Some of the methyl (*E*)-allyl ethers exhibit longer switch-off times in TN cells, due to a high value of the ratio γ_1/κ, than those of analogous liquid crystal materials incorporating either a methyl propyl ether or a 1-(*E*)-propenyl chain instead of the methyl (*E*)-allyl ether chain, see § 2.3. However, they are still useful components for nematic mixtures, especially where a wide temperature range is required or a steep contrast curve is required due to the high elastic constant ratio k_{33}/k_{11}. The higher degree of linearity and rigidity of the methyl (*E*)-allyl ether chain is probably the cause of these effects [51, 52].

2.3. *trans-4-Substituted-cyclohexyl (E)-alk-2-enoates*

Compounds containing a terminal chain incorporating an *ester* group (COO) and a carbon–carbon double bond, i.e. the (*E*)-alk-2-enoyloxy group ($C_nH_{2n+1}CH{=}CHCOO$) and especially the (*E*)-2-but-enoyloxy moiety ($CH_3CH{=}CHCOO$) generally exhibit a high T_{NI} (e.g. **33**, see table 4), especially when compared to the corresponding aliphatic esters without an additional carbon–carbon double bond (e.g. **32**, see table 4) [53, 54]. The fact that the butanoate (**32**) without a carbon–carbon double bond is not mesomorphic, while the corresponding (*E*)-but-2-enoate (**33**) with a *trans*-carbon–carbon double bond exhibits a T_{NI} at a much higher temperature than that of the reference benzonitrile (**17**), illustrates once more how complex the relationship is between structure and transition temperatures.

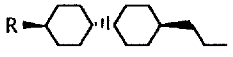
This is illustrated by the thermal data in table 9, where the effect of systematically introducing oxygen atoms (O) and double bonds (C=O and C=C) into the fully aliphatic compound (**50**) [53], to yield the intermediate products (**51–53**) [42, 53, 56] and finally the (*E*)-but-2-enoate (**54**) [53], on the transition temperatures is shown. Increasing the polarity of the chain by introducing an oxygen atom or a ketone group (C=O) does not induce a nematic phase. The added stiffness (i.e. the reduced number of non-linear conformations) and increased dispersion forces due to the presence of the carbon–carbon double bond in the chain give rise to a nematic phase at high temperatures. However, a smectic B phase is still present, also at high temperatures. Only the combination of all these elements to produce the (*E*)-but-2-enoate (**54**) yields a very high T_{NI} and a wide nematic phase without an observable smectic phase. The effects of individual building blocks (e.g. oxygen atoms, double bonds, etc.) on the transition temperatures are clearly not additive. Therefore, some co-operative effects due to the combination of exactly these groups in these positions and configurations must be respons-

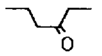
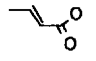
Table 8. Transition temperatures for the methyl (*E*)-[*trans*-4-(*trans*-4-alkenylcyclohexyl)cyclohexyl]allyl ethers (**46–49**).



Compound	R	Cr–S_B/N/°C	S_B–N/I/°C	N–I/°C	$\Delta T_{N\text{-}I}$/°C	Reference
46		9	18	36	18	[52]
45		10	–	92	82	[52]
47		−17	67	75	8	[52]
48		39	71	100	29	[52]
49		13	89	–	–	[52]

Table 9. Transition temperatures for the *trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl-substituted compounds (**50–54**).



Compound	R	Cr–S_B/N/°C	S_B–N/I/°C	N–I/°C	ΔT_{N-I}/°C	Reference
50		23	96	–	–	[53]
51		32	74	–	–	[56]
52		56	92	–	–	[53]
53		44	75	96	21	[42]
54		77	–	172	95	[53]

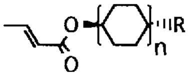
ible. There is no conjugation between the ester group and the cyclohexane ring. Thus, the explanations given for the aromatic alkenoates [57, 58], see §2.7, which invoke a high degree of conjugation between the double bond, the ester function and the adjacent benzene ring cannot be valid for alicyclic, e.g. cyclohexyl, alkenoates.

The diester (**58**), see table 10, is symmetrical and the dielectric anisotropy may be assumed to be close to zero. Due to the aliphatic nature of the molecular core, the molecular polarizability is also probably not considerable. The resultant dipole of the carboxy group of the other aliphatic (mono) ester (**57**) is at an angle to the molecular axis. Therefore, the dielectric anisotropy will also be close to zero and may even be negative. Thus, the very high T_{NI} and wide nematic ranges of such esters are very difficult to explain using the Maier–Saupe theory of the nematic phase [1]. Hard rod theories [2] which neglect all attractive forces would not explain the differences in T_{NI} for isomers, which are almost identical in shape, incorporating oxygen atoms at different positions in the chain, e.g. compounds (**30** and **31**), see table 4, or in the linkage [49, 50]. Although the Boltzmann distribution of the various conformers of the two chains of the ethers (**30** and **31**) may be responsible for the differences in mesomorphic behaviour, this is less likely for compounds incorporating dipoles in the central linkage, where the difference in T_{NI} can be considerable (>150°C) [49, 50]. This would presume a bent, non-linear conformation of the molecule. Combined theories [3–6] or theories modified for strong intermolecular dipole–dipole interactions may be more appropriate.

It is evident from the thermal data collated in table 10 that at least two rings are required for mesophase formation, despite the high nematic tendencies of the benzonitriles incorporating the (*E*)-but-2-enoyloxy moiety [53]. Despite the very high T_{NI} of the two-ring ester (**56**), the one ring (*E*)-but-2-enoate (**55**) and (*E*)-but-2-enoate (**57**) do not exhibit mesomorphic behaviour. The replacement of the propyl chain in the two-ring mono-ester (**56**) by an (*E*)-but-2-enoyloxy chain to yield the di-ester (**58**) results in an increase in the already high T_{NI}. This would suggest that a central core of at least two rings is necessary for mesophase formation above room temperature. However compounds with no ring at all or with only one ring have been found to form liquid crystals [26–28, 32]. The nematic phases observed for simple unsaturated aliphatic acids, see table 2, (with two *trans*-double bonds and no rings [32]) can be rationalized by invoking stabilization effects due to increased rigidity of the terminal chain. However, on the basis of these explanations a mesophase could have been expected for at least one of the one-ring (*E*)-but-2-enoates (**55** and **57**).

The effect of replacing one of the cyclohexane rings

Table 10. Transition temperatures for the *trans*-4-substituted cyclohexyl (*E*)-but-2-enoates (**55–58**).



Compound	R	*n*	Cr–N/I/°C	N–I/°C	ΔT_{N-I}/°C	Reference
55	C_3H_7	1	<25	–	–	[53]
56	C_3H_7	2	77	172	95	[53]
57	$CH_3CH{=}CHCO_2$	1	93	–	–	[53]
58	$CH_3CH{=}CHCO_2$	2	168	202	34	[53]

in the (*E*)-but-2-enoate (**56**) with a benzene ring to produce the (*E*)-but-2-enoate (**59**) is shown clearly in table 11. Although the T_m values are similar, the T_{NI} of the phenyl substituted ester (**59**) is lower, resulting in the formation of a monotropic nematic phase. Increasing the polarity by replacing one methylene unit in the propyl chain by an oxygen atom to yield the (*E*)-but-2-enoate (**61**) leaves T_m almost unchanged, but increases the T_{NI} considerably, resulting in an enantiotropic nematic phase. The effect is normal, but unusually large. Introduction of an additional cyclohexane ring into the two-ring (*E*)-but-2-enoate (**61**) to yield the three-ring (*E*)-but-2-enoate (**62**) increases the T_m slightly, but increases the T_{NI} drastically. As no smectic mesomorphism could be observed, this results in an unusually wide range nematic phase.

The direct dependence of the physical properties of four strongly related compounds on small differences in the steric and polar effects of the terminal chains is shown by reference to figures 1–7 [54]. The four difluoro-substituted liquid crystal materials incorporate the (*E*)-methoxypropenyl (code: $101d_1CCP_FF$), the methoxypropyl (code: $103CCP_FF$), the 1-(*E*)-propenyl chain (code; $1d_1CCP_FF$) and the (*E*)-but-2-enoyloxy (code: $1d_3ECCP_FF$) terminal groups. Binary mixtures are required in order that measurements can be carried out in the temperature range of the instruments [54]. The binary mixtures M1–4 are formed from a weakly polar standard nematogen (*E*)-3-pentenyl 4-(*trans*-4-propylcyclohexyl)phenyl ether (code: $3CPOd_31$) and the four difluoro-substituted (polar) bicyclohexanes [54].

The mixtures M1–4 exhibit broadly similar plots of the elastic constants ($k_{ii} = k_{33}$, k_{22} and k_{11}) against reduced temperature (T/T_{NI}), see figure 1. Therefore, the plots of the ratios k_{33}/k_{11} and k_{22}/k_{11} against T/T_{NI} for the binary mixtures are also similar, see figures 2 and 3. The values of the elastic constants k_{33} and k_{22} are highest and k_{11} is the lowest for mixtures containing the ester (code; $1d_3ECCP_FF$). This non-linear behaviour results in steep voltage–transmission characteristics in STN-LCDs, where high values of k_{33}/k_{11} are required [10–14].

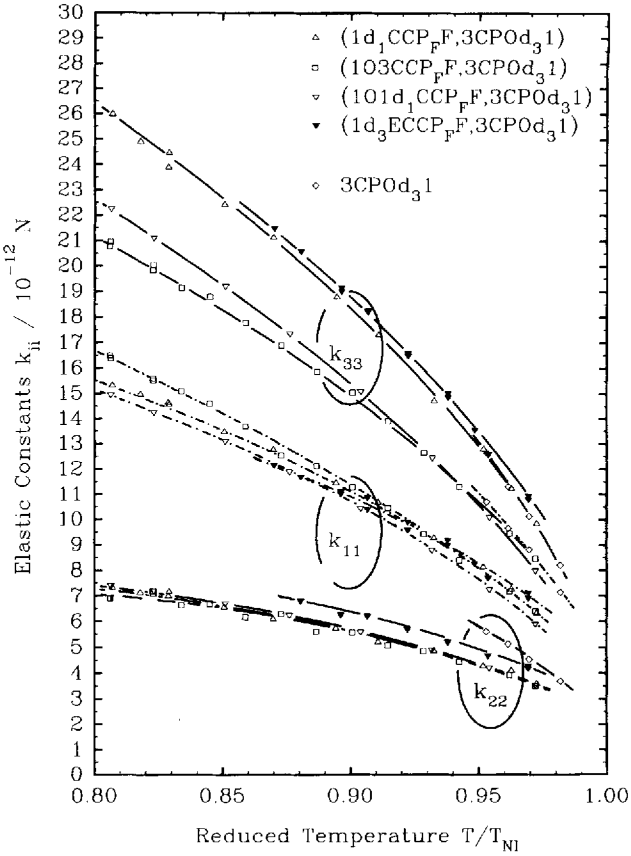
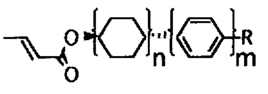


Figure 1. Plots of the elastic constants k_{ii} against reduced temperature T/T_{NI} for the pure compound $3CPOd_31$ and the binary mixtures $1d_1CCP_FF/3CPOd_31$, $103CCP_FF/3CPOd_31$ $101d_1CCP_FF/3CPOd_31$ and $1d_3ECCP_FF/3CPOd_31$.

The plots and also the absolute values of κ against $1/T$ for the four mixtures are similar, see figure 4. The elastic expression κ and $\Delta\varepsilon$ determine the threshold voltage of twisted nematic TN-LCDs [42, 43]. $\Delta\varepsilon$ of the mixture M4 containing the ester $1d_3ECCP_FF$ is the second lowest for the four mixtures. This indicates a lateral contribution from the ester (carboxy) group as is

Table 11. Transition temperatures for the *trans*-4-substituted cyclohexyl (*E*)-but-2-enoates (**59–62**).



Compound	R	*n*	*m*	Cr-N/I/°C	N-I/°C	ΔT_{N-I}/°C	Reference
59	C_3H_7	1	1	71	47[a]	–	[53]
60	C_3H_7	2	0	77	172	95	[53]
61	OC_2H_5	1	1	78	110	32	[53]
62	OC_2H_5	2	1	86	275	189	[53]

[a] Represents a monotropic transition temperature.

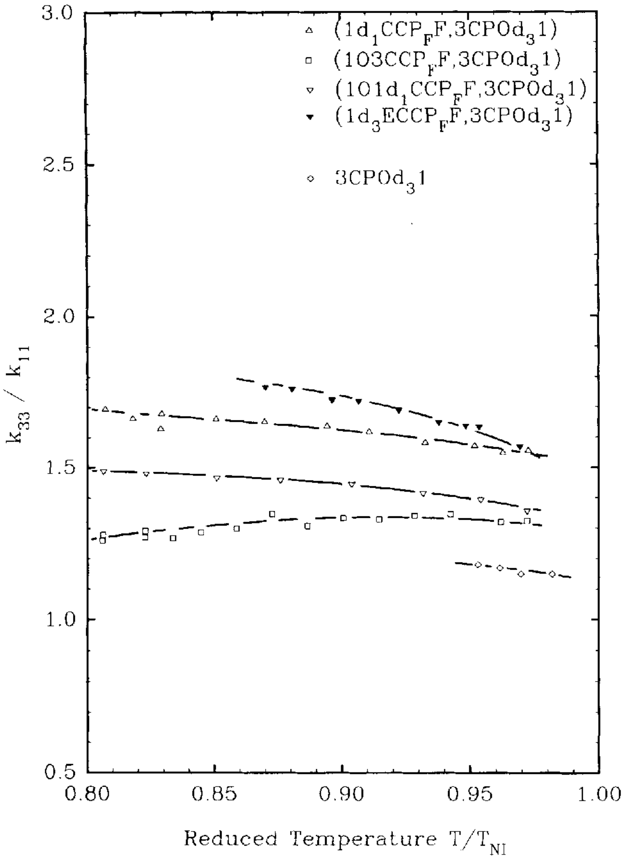


Figure 2. Plots of the elastic constant ratio k_{33}/k_{11} against reduced temperature T/T_{NI} for the pure compound 3CPOd$_3$1 and the binary mixtures 1d$_1$CCP$_F$F/3CPOd$_3$1, 103CCP$_F$F/3CPOd$_3$1 101d$_1$CCP$_F$F/3CPOd$_3$1 and 1d$_3$ECCP$_F$F/3CPOd$_3$1.

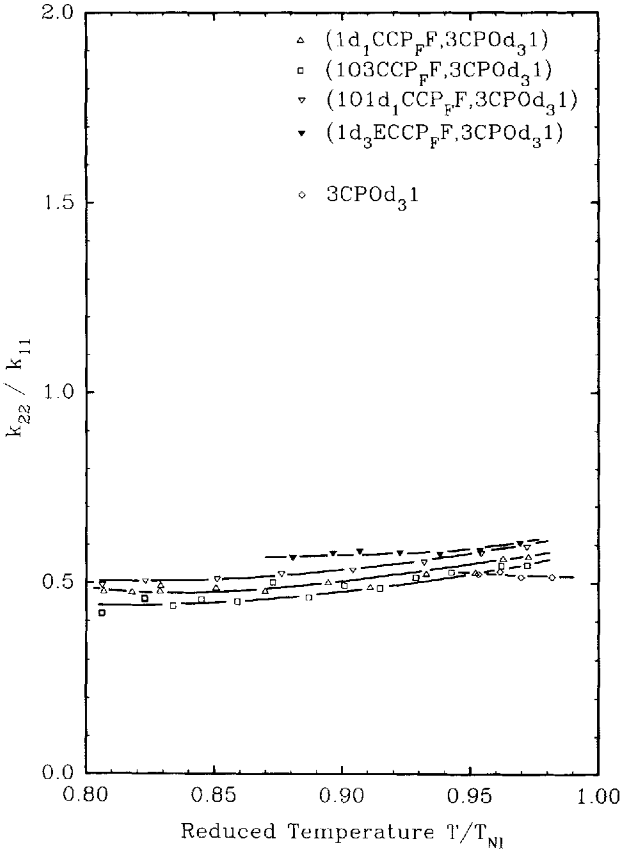


Figure 3. Plots of the elastic constant ratio k_{22}/k_{11} against reduced temperature T/T_{NI} for the pure compound 3CPOd$_3$1 and the binary mixtures 1d$_1$CCP$_F$F/3CPOd$_3$1, 103CCP$_F$F/3CPOd$_3$1 101d$_1$CCP$_F$F/3CPOd$_3$1 and 1d$_3$ECCP$_F$F/3CPOd$_3$1.

seen in the value for $\varepsilon_\perp$. This combination of κ and $\Delta\varepsilon$ results in the highest threshold voltage for the mixture containing the ester.

The plot of the rotational viscosity γ_1 against $1/T$ of the mixture M4 containing the ester 1d$_3$ECCP$_F$F, as shown in figure 5, is higher than those of the other mixtures M1–M3. This is not surprising, as esters normally possess a higher γ than alkanes or ethers. Although comparisons of viscosity and viscoelastic ratios should be made at constant temperatures (e.g. 22°C), this is not possible in this case due to crystallization problems close to room temperature. However, the general trends observed at higher (reduced) temperatures are certainly indicative of the behaviour at room temperature.

The plots of the viscoelastic ratio γ_1/κ of all the binary mixtures have a very similar shape, see figure 6. The values for the binary mixture M4 containing the ester 1d$_3$ECCP$_F$F are a little higher than those of the other binary mixtures M1–M3. The ratio γ_1/κ essentially determines the switch off times, $t_{off} \propto \gamma_1/\kappa$ in TN-LCDs cells.

The ratio γ_1/κ and thus t_{off} are similar for the two binary mixtures M1 and M2 incorporating the compounds 101d$_1$CCP$_F$F and 103CCP$_F$F with an oxygen atom in the chain, see figures 6 and 7. The response times of the mixture M3 incorporating the (*E*)-propenyl-substituted compound (1d$_1$CCP$_F$F) are shorter due to the smaller chain length. However, the unusually low value for the mixture M4 incorporating the ester (1d$_3$ECCP$_F$F) cannot be rationalized in this way, see figure 7. The absolute values and ratios of the physical properties of all of the compounds containing a carbon–carbon double bond render them more than suitable as components of nematic mixtures for STN-LCD applications [54].

2.4. *Alkyl (E)-(trans-4-Substituted-cyclohexyl)acrylates*

The thermal data collated in table 12 for the propriolate (**63**) and the acrylates (**64** and **65**) show that the combination of two *trans*-carbon–carbon double bonds and the dipole moment associated with the ester group

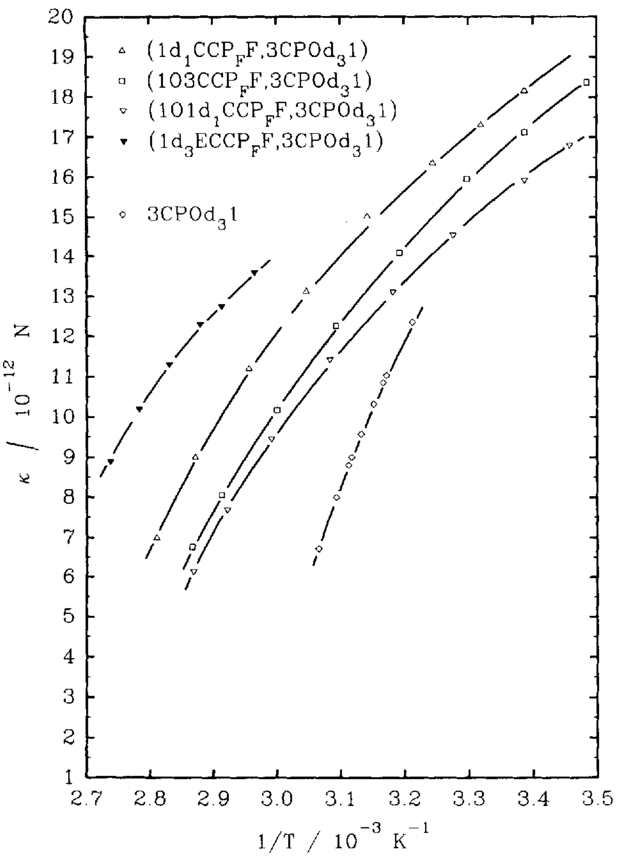


Figure 4. Plots of the elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ against the temperature reciprocal for the pure compound 3CPOd$_3$1 and the binary mixtures 1d$_1$CCP$_F$F/3CPOd$_3$1, 103CCP$_F$F/3CPOd$_3$1 101d$_1$CCP$_F$F/3CPOd$_3$1 and 1d$_3$ECCP$_F$F/3CPOd$_3$1.

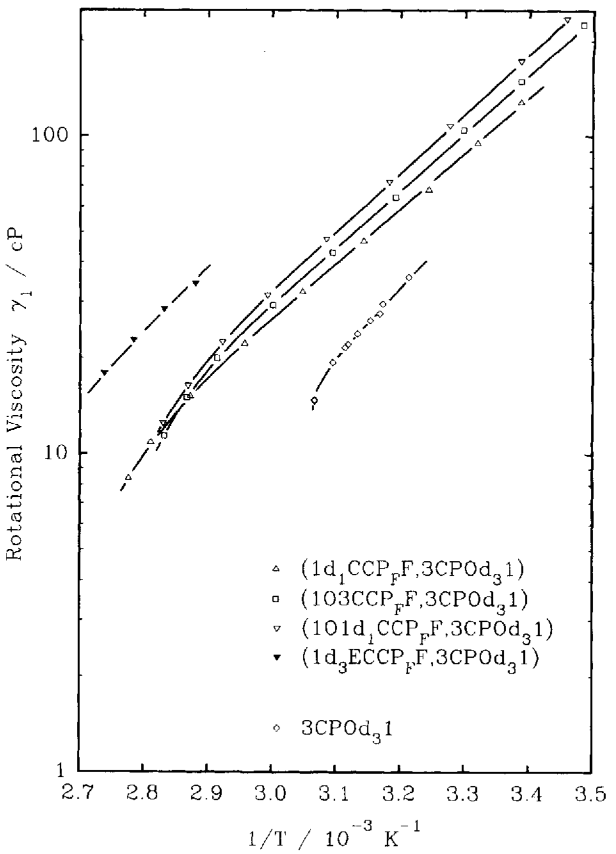


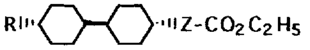
Figure 5. Plots of the rotational viscosity γ_1 against the temperature reciprocal for the pure compound 3CPOd$_3$1 and the binary mixtures 1d$_1$CCP$_F$F/3CPOd$_3$1, 103CCP$_F$F/3CPOd$_3$1 101d$_1$CCP$_F$F/3CPOd$_3$1 and 1d$_3$ECCP$_F$F/3CPOd$_3$1.

results in broad nematic mesophases with a high T_{NI} for two-ring compounds [52]. The transition temperatures of a number of ethyl (*E*)-(*trans*-4-[*trans*-4-alkenyl cyclohexyl]cyclohexyl)acrylates (**63–69**) recorded in tables 12 and 13 indicate that this combination strongly suppresses the smectic B phase in favour of the nematic phase. Even the acrylate (**69**) with a terminal double bond, known to promote smectic phases, still exhibits a nematic phase above the smectic B phase [52]. These results reveal that the incorporation of dipoles in the form of hetero-atoms and double bonds of a defined configuration into a substance possessing only smectic phases can convert the mesomorphic behaviour to nematic. However, the high viscosity found for these acrylates precludes their use in normal LCDs, where short response times are essential.

2.5. *Halovinyl compounds*

The effect of introducing a dipole moment along the molecular axis in a terminal position of a 1-propenyl

Table 12. Transition temperatures for the ethyl esters (**63–65**) below.



Compound	R	Z	Cr–S$_B$/N/°C	S$_B$–N/°C	N–I/°C	ΔT_{N-I}/°C	Reference
63			38	64	–	–	[52]
64			32	–	76	44	[52]
65			39	–	94	55	[52]

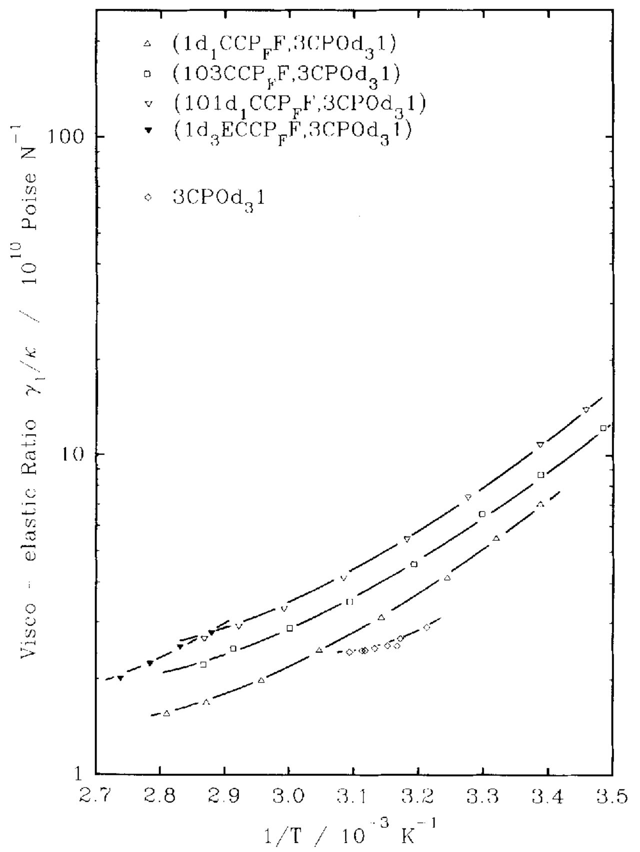


Figure 6. Plots of the viscoelastic ratio γ_1/κ against the temperature reciprocal for the pure compound 3CPOd$_3$1 and the binary mixtures 1d$_1$CCP$_F$F/3CPOd$_3$1, 103CCP$_F$F/3CPOd$_3$1 101d$_1$CCP$_F$F/3CPOd$_3$1 and 1d$_3$ECCP$_F$F/3CPOd$_3$1.

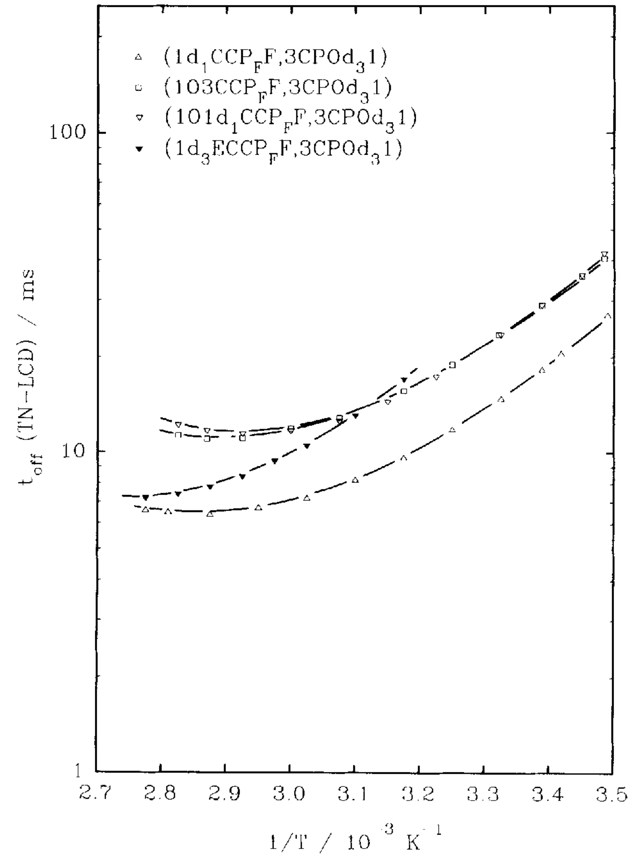
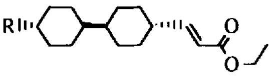


Figure 7. Plots of the switch off times t_{off} against the temperature reciprocal for the binary mixtures 1d$_1$CCP$_F$F/3CPOd$_3$1, 103CCP$_F$F/3CPOd$_3$1 101d$_1$CCP$_F$F/3CPOd$_3$1 and 1d$_3$ECCP$_F$F/3CPOd$_3$1.

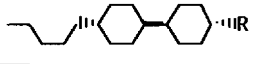
chain of a bicyclohexyl compound (**71**) to produce the corresponding halovinyl compound (**72**) is shown in table 14. The fluorovinyl substituted material (**72**) [59] possesses a lower T_{m}, smectic B transition temperature and T_{NI} than the corresponding alkenyl compound (**71**). However, the corresponding totally saturated substance (**70**) only exhibits a smectic B phase. The addition of a second fluorine atom in a terminal position on the double bond eliminates the problem of *cis*-/*trans*-separation and purification, but T_{NI} and $\Delta\varepsilon$ are reduced significantly and γ can be supposed to be increased. These fluorovinyl substituted materials and related chlorovinyl [60] substituted compounds exhibit intermediate $\Delta\varepsilon$

Table 13. Transition temperatures for the ethyl (*E*)-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]acrylates (**66**–**69**).



Compound	R	Cr–S$_B$/N/°C	S$_B$–N/°C	N–I/°C	$\Delta T_{\mathrm{N-I}}$/°C	Reference
66		2	–	43	41	[52]
65		39	–	94	55	[52]
67		15	–	80	65	[52]
68		34	–	94	60	[52]
69		7	44	70	26	[52]

Table 14. Transition temperatures for the *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl-substituted compound (**70–72**).



Compound	R	Cr–S_B/°C	S_B–N/I/°C	N–I/°C	ΔT_{N-I}/°C	Reference
70		23	96	–	–	[53]
71		38	73	95	22	[53]
72		−2	49	62	13	[59]

values useful for reducing the threshold voltage in nematic mixtures of high resistivity for actively addressed LCDs (e.g. TFT-LCDs). Many chlorovinyl substituted compounds possess a nematic phase at high temperatures [60]. The high T_{NI} values of these compounds allow the incorporation of several lateral substituents, especially fluorine atoms, into the core of the molecule in order to produce a higher $\Delta\varepsilon$ without complete elimination of the nematic phase [60]. Thus, it is not necessary to resort to the use of polar terminal groups such as the cyano group, which are known to lead to insufficiently high resistivity values for actively-addressed LCDs [8, 9].

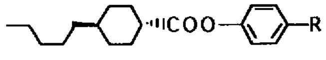
2.6. *Alkenyloxy-substituted compounds*

A carbon–carbon double bond at or beyond position 3 in an alkenyl or alkenyloxy chain attached to an aromatic ring is also non-conjugated and therefore sufficiently stable for LCD applications. Similar effects to those observed in an alkenyl chain attached to cyclohexane rings are found for alkenyloxy compounds (**76** and **78**), see table 15 [61, 62]. It is evident that the incorporation of a *trans*-double bond at position 3 and 4 in the pentyl or pentyloxy chain of the esters (**73** and **74**) [62] to yield a number of phenyl *trans*-4-pentylcyclohexanoates (**75** and **76**) [61], differing only in the nature of the group R, leads to a significant increase in T_{NI}. The introduction of a terminal double bond into the esters (**75** and **76**) to yield the esters (**77** and **78**) leads to a decrease in T_{NI} in both cases, as is generally observed.

A carbon–carbon double bond was introduced in a terminal position or in a *cis*-configuration in the middle of an alkoxy chain of a wide variety of phenyl benzoates [63–66] and phenylpyrimidines [67], which exhibit a chiral smectic C phase. In all cases, this often led to a substantial decrease in the transition temperatures of all the observed mesophases. However, T_m was often decreased more than T_{S_C} leading to a broadening of the smectic C temperature range (sometimes at or just above room temperature). The ester group and/or chain branching at the chiral centre led to a high γ and relatively long τ [68].

More significant changes in the transition temperatures and other physical properties of relevance for FLCDs were observed for non-chiral, alkenyloxy-substituted phenylpyrimidines/pyridines [69–74], where the position and configuration of the double bond were varied systematically, see table 16 and figures 8 and 9 for the ethers (**79–92**). The *trans*-carbon–carbon double bond at an even number of carbon atoms from the molecular core results generally in a higher T_{S_C}, lower smectic A transition temperatures, an increase in θ and P_s and in longer τ. A *cis*-double bond at an odd number of carbon atoms from the molecular core suppresses the

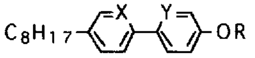
Table 15. Transition temperatures for the 4-substituted-phenyl *trans*-4-pentylcyclohexanoates (**73–78**).

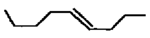
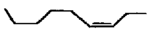
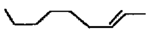
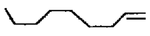
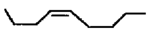
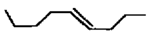
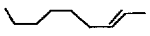
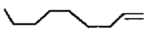


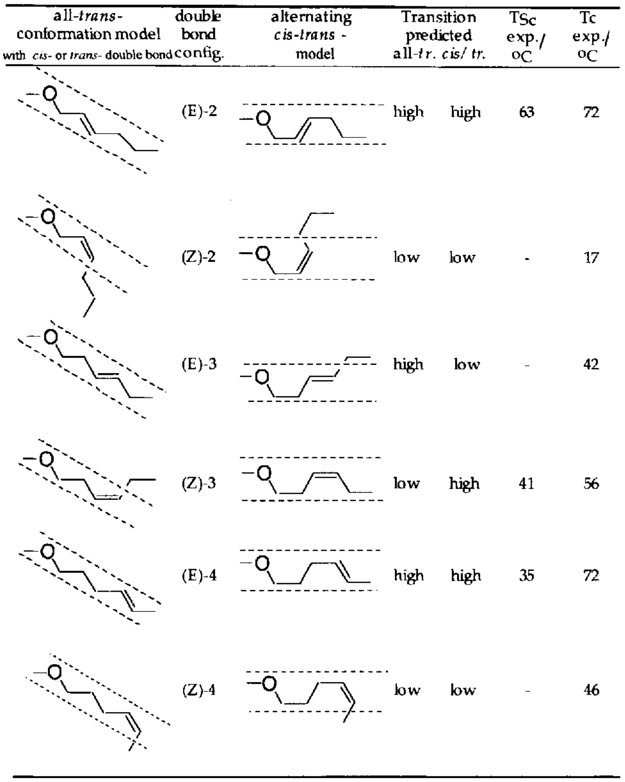
Compound	R	Cr–N/I/°C	N–I/°C	ΔT_{N-I}/°C	Reference
73		36	48	12	[62]
74		49	81	32	[62]
75		42	75	33	[61]
76		48	93	45	[61]
77		33	22^a	–	[61]
78		35	62	27	[61]

[a] Represents a monotropic transition temperature.

Table 16. Transition temperatures of the 2-[4-octyloxyphenyl]-5-octylpyridine (**79**), 2-[4-(octenyloxy)phenyl]-5-octylpyridines (**80–85**), 2-(4-octylphenyl)-5-octyloxypyridine (**86**) and 2-(4-octylphenyl)-5-(octenyloxy)pyridines (**87–92**).

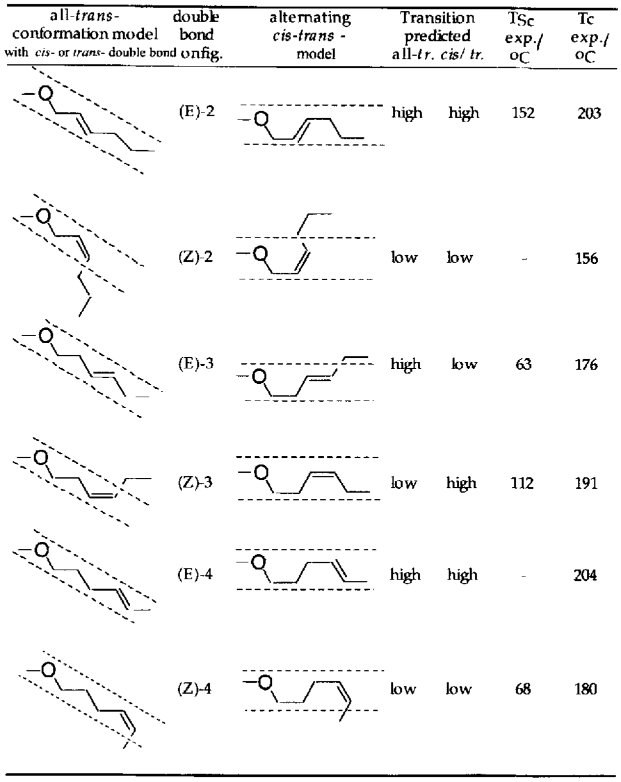


Compound		R	X	Y	Cr–G/S_I/S_C/°C	G–S_I/°C	S_I–S_C/I/°C	S_C–S_A/I/°C	S_A–I/°C	Reference
79			N	CH	38	–	62	82	–	[71]
80	(*E*)		N	CH	43	57	75	85	–	[71]
81	(*Z*)		N	CH	11	–	40	61	–	[71]
82	(*E*)		N	CH	61	72	84	85	–	[71]
83	(*Z*)		N	CH	16	–	60	67	–	[71]
84	(*E*)		N	CH	36	–	66	80	–	[71]
85			N	CH	23	–	53	75	–	[71]
86			CH	N	24	–	65	81	87	[73]
87	(*E*)		CH	N	25	–	72	84	–	[73]
88	(*Z*)		CH	N	−15	−9	56	–	–	[73]
89	(*E*)		CH	N	<20	–	78	86	–	[73]
90	(*Z*)		CH	N	−18	−11	64	–	65	[73]
91	(*E*)		CH	N	25	67	–	70	86	[73]
92			CH	N	34	–	51	68	79	[73]



all-*trans*-conformation model with *cis*- or *trans*- double bond config.	double bond	alternating *cis-trans* - model	Transition predicted all-*tr.*	Transition predicted *cis*/ *tr.*	TSc exp./ °C	Tc exp./ °C
	(E)-2		high	high	63	72
	(Z)-2		low	low	-	17
	(E)-3		high	low	-	42
	(Z)-3		low	high	41	56
	(E)-4		high	high	35	72
	(Z)-4		low	low	-	46

Figure 8. Two possible notations that model the conformations of the hexenyloxy chain of the two-ring ethers [73]: on the left it is seen that the all-*trans*-model leads, for every position of the double bond, to the straightest chain and the highest smectic C transition temperature T_{S_C} (S_C–S_A) and clearing point T_c (S_A–I or N–I). The alternating *cis-trans*-notation also predicts higher values for T_{S_C} and T_c for the (*Z*)-hex-3-enyloxy-substituted ether than for the (*E*)-hex-3-enyloxy-substituted ether, as is observed experimentally.



all-*trans*-conformation model with *cis*- or *trans*- double bond config.	double bond	alternating *cis-trans* - model	Transition predicted all-*tr.*	Transition predicted *cis*/ *tr.*	TSc exp./ °C	Tc exp./ °C
	(E)-2		high	high	152	203
	(Z)-2		low	low	-	156
	(E)-3		high	low	63	176
	(Z)-3		low	high	112	191
	(E)-4		high	high	-	204
	(Z)-4		low	low	68	180

Figure 9. Two possible notations that model the conformations of the hexenyloxy chain of the three-ring ethers [73]: on the left it can be seen that the all-*trans*-situation leads, for every position of the double bond, to the straightest chain and the highest smectic C transition temperature T_{S_C} (S_C–S_A) and clearing point T_c (S_A–I or N–I). The alternating *cis-trans*-notation also predicts higher values for T_{S_C} and T_c for the (*Z*)-hex-3-enyloxy-substituted ether than for the (*E*)-hex-3-enyloxy-substituted ether, as is observed experimentally.

nematic phase in favour of smectic phases, decreases θ and P_s and shortens τ. Other positional combinations strongly reduce the transition temperatures. These observations were related to a linear, alternately *trans-cis*-configuration and conformation of the alkenyloxy chain [70, 73, 74]. However, the position and number of nitrogen atoms are also crucial in determining the type of phases observed, their absolute transition temperatures and temperature ranges. Similar, if not identical, trends have been found for related three-ring fully aromatic ethers, as well as ethers incorporating cyclohexane [64–68] or dioxane rings [75] in place of one of the phenyl rings.

The dependence of transition temperatures, P_s, γ and τ on small differences in the position and configuration of double bonds and nitrogen atoms for structurally similar compounds exhibiting a smectic C phase is demonstrated by reference to data for mixtures of the ethers (**80**–**85** and **87**–**92**) in a standard chiral smectic C mixture as shown in figures 10 and 11. The transition temperatures of both series of mixtures possess an odd–even effect. The values for those mixtures containing ethers (**81**, **83**, **85**, **88**, **90** and **92**) with a *cis*- or a terminal double bond (even positions) are lower than those for the mixtures incorporating ethers (**80**, **82**, **84**, **87**, **89** and **91**) with a *trans*-double bond. This reflects the trends in the transition temperatures of the pure compounds, see table 16. P_s and τ show only a weak dependence on the position of the double bond. This dependence is related to the corresponding variation of the chiral smectic C–smectic A transition temperatures. While the average values for transition temperatures and P_s are similar for both isomer series, τ for the mixtures containing the ethers (**87**–**92**) is lower for most mixtures, see figures 10 and 11. This indicates a substantially lower viscosity γ for the ethers (**87**–**92**) with the alkenyloxy chain attached to the pyridine ring.

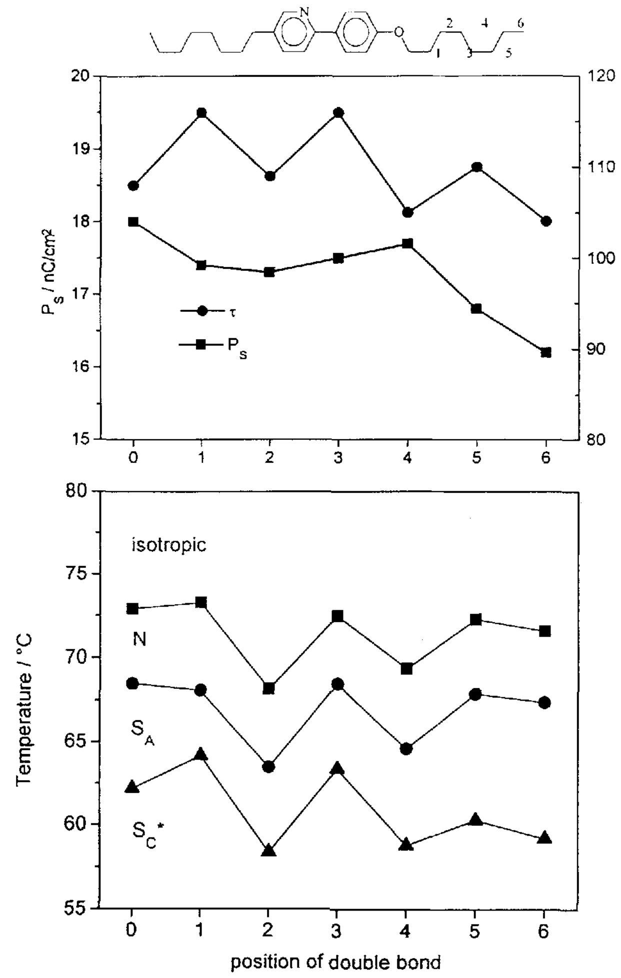


Figure 10. Plot of the transition temperatures, spontaneous polarization (P_s) and switching times (τ) of the mixtures containing 15 wt % of the ethers (**80–85**)—see Table 16—and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position of the carbon–carbon double bond in the octenoyloxy chain; 0 indicates no double bond in the chain.

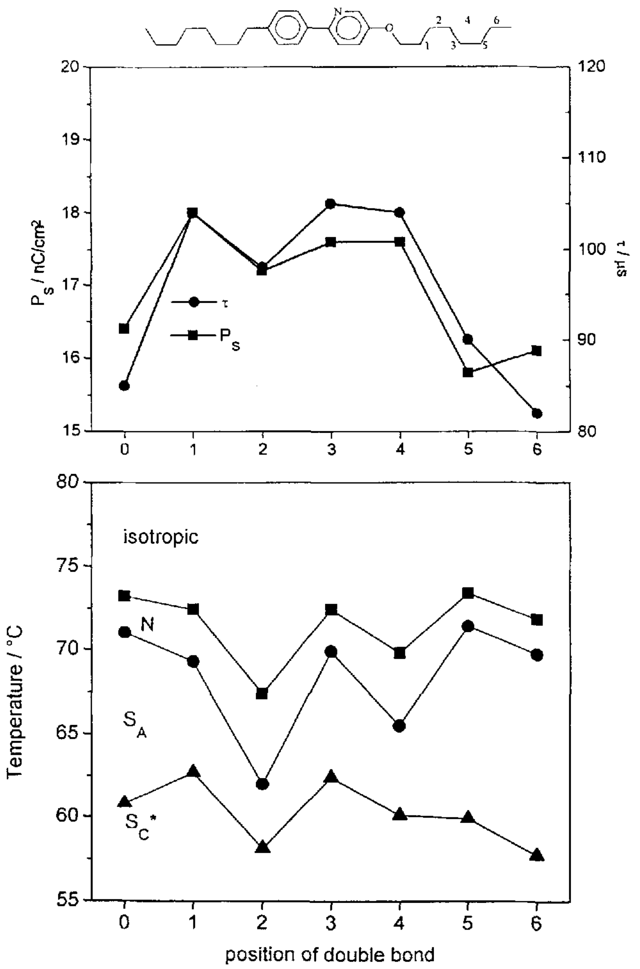
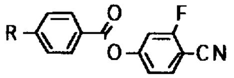


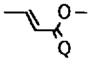
Figure 11. Plot of the transition temperatures, spontaneous polarization (P_s) and switching times (τ) of the mixtures containing 15 wt % of the ethers (**87–92**)—see Table 16—and 85 wt % of the chiral smectic C mixture SCO 1014 versus the position of the carbon–carbon double bond in the octenoyloxy chain; 0 indicates no double bond in the chain.

2.7. *Aromatic alkenoates*

It has been known for a long time that a small number of aromatic esters of (*E*)-alk-2-enoic acids exhibit very high T_{NI} [57, 58]. Although this had been explained in terms of a high degree of polarizability due to conjugation between the carboxy (ester) group, the carbon–carbon double bond and the benzene ring [57, 58], this cannot fully explain these results as shown in § 2.3. This is exemplified by more recent results [76–79] as shown in table 17 for a number of esters (**93–97**) of very high [80–83] more recently. The transition temperatures for each position of the double bond were lowered compared to those of the corresponding alkanoates without a double bond in the terminal chain. This contrasts with the situation seen for the corresponding alkenyl ethers, see table 16. The general trends in the transition temperatures of the alkanoates and alkenoates investigated are complicated and, although generally valid, there are several exceptions to them. This is especially true for the (*E*)-alk-2-enoates where the divergence from general

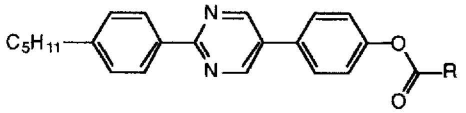
Table 17. Transition temperatures for the 4-cyano-3-fluorophenyl 4-substituted-benzoates (**93–97**).



Compound	R	Cr–N/I/°C	N–I/°C	$\Delta T_{N\text{–}I}$/°C	Reference
93		31	25^a	–	[76, 77]
94		72	49^a	–	[76, 77]
95		39	–	–	[78]
96		43	5^b	–	[78]
97	(*E*) 	125	195	70	[79]

[a] Represents a monotropic transition temperature.
[b] Represents a virtual (extrapolated) transition temperature.

Table 18. Transition temperatures for the 4-(5-[4-pentylphenyl]pyrimidin-2-yl)phenyl butanoate (**98**) and 4-(2-[4-pentylphenyl[pyrimidin-5-yl)phenyl (*E*)-but-2-enoate (**99**).



Compound	R	Cr–S_C/°C	S_C–S_A/N/°C	S_A–N/°C	N–I/°C	Reference
98		143	170	225	229	[83]
99	(*E*) 	146	162	–	270	[83]

but-2-enoate (**99**) does not possess a smectic A phase and T_{NI} is much higher. Hence, in special cases (this is not typical of the general effect) the nature and absolute transition temperatures of the phases observed can be influenced to a greater extent than is usually observed for this manipulation. This reflects the very complex intra-/inter-molecular interactions responsible for the observed transition temperatures [84–86].

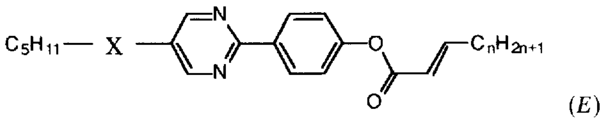
The differences between the transition temperatures of the 4-(5-nonylpyrimidin-2-yl)phenyl (*E*)-alk-2-enoates (**100–108**) [82] and the 4-(5-[4-pentylphenyl]pyrimidin-2-yl)phenyl (*E*)-alk-2-enoates (**109–117**) [83], differing only in the presence of an additional 1,4-disubstituted phenylene ring for the latter, are shown in table 19. All the two-ring esters (**100–108**) exhibit a nematic phase at high temperatures for apolar two-ring compounds and no observable smectic mesomorphism. In comparison, the three-ring esters possess wide-range smectic C and A as well as nematic phases at high temperatures. T_{NI} is increased much more than T_m, as usual. This must be due to the greater length/breadth ratio and the associated higher degree of molecular polarizability resulting from the additional 1,4-disubstituted phenylene ring. These two- and three-ring (*E*)-alken-2-enoates, as well as other alkenoates with the double bond or nitrogen atoms in different positions, despite the pure nematic nature of the former, induce a high T_{S_C} and a low γ in mixtures with other smectic C materials and a chiral dopant [82, 83].

3. Carbon–carbon double bonds in the central linkage

3.1. *Two-unit linking groups*

The effect of a *trans*-carbon–carbon double bond in the centre of the molecular core of a mesogen [87–89] is shown in tables 20 and 21. The introduction of a double bond into the apolar smectic compound (**118**) to yield the compound (**119**) does not change the mesomorphism greatly [87], whereas the presence of a carbon–carbon triple bond in the compound (**120**) results in the formation of a monotropic nematic phase. The danger of extrapolating from one system to another is illustrated by reference to the thermal data collated in table 21. The polar nematic compound (**122**) with a double bond in the molecular core exhibits a higher T_{NI}, lower T_m and thus a broader nematic range than the

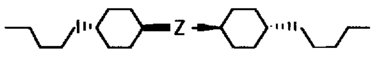
Table 19. Transition temperatures for the 4-(5-nonylpyrimidin-2-yl)phenyl (*E*)-alk-2-enoates (**100–108**) and 4-(5-[4-pentylphenyl]pyrimidin-2-yl)phenyl(*E*)-alk-2-enoates (**109–117**).

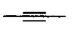


Compound	X	*n*	Cr–S_C/S_A/N/I/°C	S_C–S_A/N/°C	S_A–N/°C	N–I/°C	Reference
100	$-C_4H_8-$	1	80	–	–	89	[82]
101	$-C_4H_8-$	2	89	–	–	70[a]	[82]
102	$-C_4H_8-$	3	68	–	–	81	[82]
103	$-C_4H_8-$	4	47	–	–	70	[82]
104	$-C_4H_8-$	5	49	–	–	79	[82]
105	$-C_4H_8-$	6	43	–	–	76	[82]
106	$-C_4H_8-$	7	50	–	–	81	[82]
107	$-C_4H_8-$	8	43	–	–	78	[82]
108	$-C_4H_8-$	9	60	–	–	82	[82]
109	$-C_6H_4-$	1	157	–	186	260	[83]
110	$-C_6H_4-$	2	149	–	191	246	[83]
111	$-C_6H_4-$	3	131	157	183	242	[83]
112	$-C_6H_4-$	4	123	159	184	228	[83]
113	$-C_6H_4-$	5	115	165	166	230	[83]
114	$-C_6H_4-$	6	108	166	173	219	[83]
115	$-C_6H_4-$	7	106	166	–	217	[83]
116	$-C_6H_4-$	8	96	168	174	213	[83]
117	$-C_6H_4-$	9	92	166	–	209	[83]

[a] Represents a monotropic transition temperature.

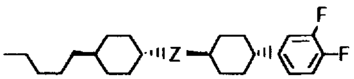
Table 20. Transition temperatures for the compounds (**118–120**).



Compound	Z	Cr–S/I/°C	S–I/°C	N–I/°C	Reference
118		46	109	–	[87]
119		53	95	–	[87]
120		52	–	50[a]	[87]

[a] Represents a monotropic transition temperature.

Table 21. Transition temperatures for the 3,4-difluorobenzenes (**121** and **122**).



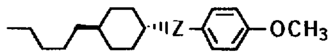
Compound	Z	Cr–N/°C	N–I/°C	ΔT_{N-I}/°C	Reference
121		38	111	73	[88]
122		31	136	105	[89]

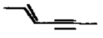
corresponding compound (**121**) without a double bond between the two cyclohexane rings [88, 89]. This is not consistent with the conclusions likely to be reached from considering the data in table 20.

3.2. *Four-unit linking groups*

The transition temperatures collated in tables 22 and 23 for a number of compounds (**123–127**) incorporating four-unit linking groups reveal the ability of the double

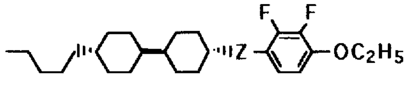
Table 22. Transition temperatures for the compounds (**123–125**).



Compound	Z	Cr-N/I/°C	S_B-I/°C	N-I/°C	ΔT_{N-I}/°C	Reference
123		27	16^a	–	–	[92]
124		25	–	34	9	[92]
125		35	–	117	82	[91]

[a] Represents a monotropic transition temperature.

Table 23. Transition temperatures for the *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexyl-substituted compounds (**126** and **127**).



Compound	Z	Cr-S_A/N/°C	S_A-N/°C	N-I/°C	ΔT_{N-I}/°C	Reference
126		49	102	138	36	[93]
127		51	–	140	89	[93]

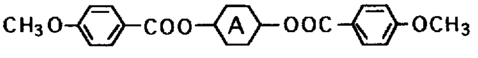
bond in a central position in the core of a mesogen to suppress smectic phases [90–93]. Although these results are not general for all homologues in these particular series [92, 93], they reveal the large differences in mesophase type and transition temperatures that can be observed for certain combinations of chain length and central linkage (butyl/(*E*)-but-3-enyl and 3-propyloxy/(*E*)-allyloxy). The relatively high γ values of many mesogens containing a four-unit linking group limits their use in LCDs. However, dopants of strong negative $\Delta\varepsilon$, as shown in table 23 [92, 93], components of moderately positive $\Delta\varepsilon$ and high resistivity [92, 93], as well as chiral dopants [94], are of commercial interest.

4. Carbon–carbon double bonds in alicyclic rings

4.1. *Cyclohexenes*

The thermal data collated in table 24 were originally cited [25, 47, 48] as confirmation of the Maier–Saupe theory, which proposed that T_{NI} should increase with increasing molecular polarizability [1]. That this is the case for these diesters (**128–131**) is evident from the thermal data collated in table 24. That the situation is much more complicated than this, as referred to earlier, is illustrated by the data [40, 95, 96] recorded in table 25 for the benzonitriles (**17**, **132**, **133**). Only the cyclohexene (**133**) with a conjugated double bond possesses a slightly higher T_{NI} than the cyclohexane (**17**). When the

Table 24. Transition temperatures for the diesters (**128–131**).



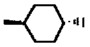
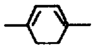
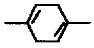
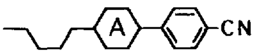
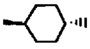
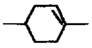
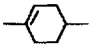
Compound	A	Cr-N/°C	N-I/°C	ΔT_{N-I}/°C	Reference
128		–	195	–	[25, 47, 48]
129		144	251	107	[25, 47, 48]
130		205	273	68	[25, 47, 48]
131		–	298	–	[25, 47, 48]

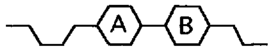
Table 25. Transition temperatures for the 4-substituted benzonitriles (**17**, **132** and **133**).



Compound	A	Cr–N/°C	N–I/°C	ΔT_{N-I}/°C	Reference
17		30	55	25	[40]
132		48	61	15	[95]
133		35	5	–	[96]

double bond is not conjugated as in the cyclohexene (**133**), the T_{NI} is much lower, although the molecular polarizability should be marginally higher, than that of the reference cyclohexane (**17**) and only somewhat lower than T_{NI} for the corresponding cyclohexene (**132**). This has been rationalized by the distorted shape of cyclohexene ring in the latter case [96]. This is almost certainly responsible for the much lower T_{NI} of the cyclohexenes (**135**–**137**) [97] compared to that of the analogous cyclohexane (**134**), see table 26. This confirms more

Table 26. Transition temperatures for the *trans*-4-alkylcyclohexyl-substituted cyclohexenes (**134**–**137**).



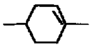
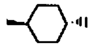
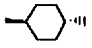
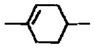
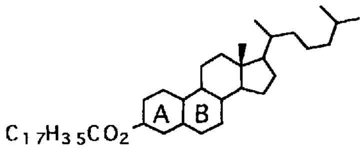
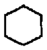
Compound	A	B	Cr–S_B/°C	S_B–N/I/°C	N–I/°C	ΔT_{N-I}/°C	Reference
134			31	97	–	–	[53]
135			–10	19	22	3	[97]
136			–11	12	27	15	[97]
137			4	21	30	9	[97]

Table 27. Transition temperatures for the steroid derivatives (**138**–**141**).



Compound	A	B	Cr–N*/I/°C	S–N*/°C	N*–I/°C	Reference
138			97	–	–	[99, 101]
139			82	–	< –20[a]	[100, 101]
140			77	–	< –20[a]	[100, 101]
141			82	74[a]	78[a]	[100–102]

[a] Represents a monotropic transition temperature.

recent theoretical explanations citing length/breadth ratios and isotropic attractive forces as the main factors responsible for mesophase formation. However, in this particular case, the smectic B phase has been strongly suppressed and a nematic phase is now observed. Similar results were obtained for esters of cyclohexene acids [98].

4.2. *Cholesterics*

A wide variety of mesogenic steroid derivatives incorporating a carbon–carbon double bond in various positions of the molecular core and the aliphatic chain have been synthesized [27, 99–102]. It is very difficult to identify any clear trends or consistent behaviour in the transition temperatures. This is partially due to the fact that data for homologues with the same chain length often do not exist or due to impurities in the compounds prepared and measured often many years ago [27]. The complexity of the situation is illustrated by the thermal data collected in table 27. In contrast to the situation observed for cyclohexanes and cyclohexenes, see §4.1, the fully saturated 3β-octadecanoyloxy-5α-cholest-1-ane (**138**) does not exhibit an observable mesophase [99]. However, other homologues of this series with shorter chain lengths do exhibit smectic and chiral nematic phases at lower temperatures than those of the corresponding 3β-octadecanoyloxy-5α-cholest-1-ene with an additional carbon–carbon double bond. The related 3β-octadecanoyloxy-5α-cholest-1-ene (**139**) and 3β-octadecanoyloxycholest-4-ene (**140**) with the carbon–carbon double bond in the same ring as the hydroxy group are also not mesomorphic [100]. Only the 3β-octadecanoyloxy-5α-cholest-1-ene (**141**) derived from cholesterol possesses observable, although monotropic, phases [102]. The acetate and benzoate of cholesta-3,4;5,6-dien-3-ol with a double bond in both rings under discussion possess smectic and chiral nematic phases. These differences have also been ascribed to geometric effects [100]. However, different sub-classes of steroid derivatives such as carbonates, thio analogues, benzoates etc., can exhibit different and apparently mutually inconsistent mesomorphic behaviour [27, 99–102]. Mesomorphism has been observed for steroid derivatives with the double bond in a variety of other positions [27, 99–102]. Chiral mesophases including the chiral smectic C phase have also been observed for esters of a non-racemic cyclohexene acid [103].

5. Conclusions

The effects of the configuration and position of a carbon–carbon double bond, sometimes in combination with dipoles, in the terminal chain of mesogens have been studied and some general trends identified, although many exceptions are still observed. An explanation of these effects beyond simple steric arguments proposing a linear, alternating *trans-cis*-conformation of the chain have yet to be forwarded. Studies of the property/structure relationships have also been carried out and the elastic ratios have been found to be of use for designing optimized mixtures for LCDs utilizing nematic or smectic liquid crystal mixtures. The situation with regards to a carbon–carbon double bond in the central linkage or core of the molecule has been investigated to a lesser extent and much remains to be done and discovered in these areas.

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References

[1] MAIER, W., and SAUPE, A., 1959, Z. *Naturf.*, **14a**, 882; 1960, Z. *Naturf.*, **15a**, 882.

[2] FLORY, P. J., and RONCA, G., 1979, *Mol. Cryst. liq. Cryst.*, **54**, 311.

[3] WARNER, M., 1987, *Mol. Cryst. liq. Cryst.*, **80**, 79.

[4] ALBEN, R., 1971, *Mol. Cryst. liq. Cryst.*, **13**, 193.

[5] COTTER, M. A., 1983, *Mol. Cryst. liq. Cryst.*, **97**, 29.

[6] COTTER, M. A., 1983, *Phil. Trans. R. Soc., London*, **A309**, 127.

[7] SCHADT, M., and HELFRICH, W., 1971, *Appl. Phys. Lett.*, **18**, 127.

[8] HOWARD, W. E., 1986, *Proc. SID*, **86**, 313.

[9] MOROZUMI, S., OHTA, T., ARAKI, R., KUBOTA, K., ONO, Y., NAKAZAWA, T., and OHARA, H., 1983, SID '84 Digest, in Japan Display '83, p. 404.

[10] SCHEFFER, T. J., and NEHRING, J., 1984, *Appl. Phys. Lett.*, **45**, 1021.

[11] KANDO, Y., NAKAGOMI, T., and HAWASAGA, S., 1985, German Patent DE-3 503 259 A1.

[12] SCHADT, M., and LEENHOUTS, F., 1987, *Proc. SID*, **28**, 275.

[13] KATOH, K., ENDO, Y., AKATSUKA, M., OHGAWARA, M., and SAWADA, K., 1987, *Jpn. J. appl. Phys.*, **26**, L1784.

[14] OKUMURA, O., NAGATA, M., and WADA, K., 1987, *ITEJ Tech. Rep.*, *11*, 27.

[15] WHITE, D. L., and TAYLOR, G. N., 1974, *J. Appl. Phys.*, **45**, 4718.

[16] WATERS, C., BRIMMEL, V., and RAYNES, E. P., 1983, *Proc. Japan Display '83*, p. 396.

[17] SCHADT, M., 1993, *Liq. Crystals*, **14**, 73.

[18] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.

[19] CLARK, N. A., HANSCHY, M. A., and LAGERWALL, S. T., 1983, *Mol. Cryst. liq. Cryst.*, **94**, 213.

[20] FÜNFSCHILLING, J., and SCHADT, M., 1991, *Jpn. J. appl. Phys.*, **30**, 741.

[21] BERESNEV, L. A., CHIGRINOV, V. G., DERGACHEV, D. I., POSHIDAEV, E. P., FÜNFSCHILLING, J., and SCHADT, M., 1989, *Liq. Cryst.*, **5**, 1171.

[22] FÜNFSCHILLING, J., and SCHADT, M., 1994, *Jpn. J. appl. Phys.*, **33**, 4950.

[23] Young, W. R., Aviram, A., and Cox, J., 1971, *Angew. Chem.*, **83**, 399.
[24] Tanguy, L., Leclercq, M., Billard, J., and Jacques, J., 1974, *Bull. Soc. Chim.*, **3–4**, 640.
[25] Dewar, M. J. S., and Riddle, R. M., 1975, *J. Am. chem. Soc.*, **97**, 6658.
[26] Vill, V., 1993, *Landolt–Börnstein*, Vol. IV/1–7 edited by J. Theime, (Berlin: Springer Verlag) and references therein.
[27] Gray, G. W., 1976, *Advances in Liquid Crystals*, Vol. 2 edited by G. H. Brown, (New York: Academic Press), p. 1 and references therein.
[28] Gray, G. W., 1974, *Crystal Growth* Vol. 1 edited by B.R. Pamplin (New York: Pergamon Press), p. 601 and references therein.
[29] Petrzilka, M., 1984, *Mol. Cryst. liq. Cryst.*, **111**, 329; 347.
[30] Takatsu, H., and Takeuchi, K., 1986, *Mol. Cryst. liq. Cryst.*, **138**, 231.
[31] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. Lett. (Paris)*, **36**, L69–L71.
[32] Maier, W., and Markau, K., 1961, *Z. phys. Chem. N.F.*, **28**, 190.
[33] Broer, D. J., Mol, G. N., and Challa, G., 1989, *Macromol. Chem.*, **190**, 19.
[34] Kelly, S., 1995, *J. Mater. Chem.*, **5**, 2047.
[35] Martins, A. F., Ferreira, J. B., Volino, F., Blumstein, A., and Blumstein, R. B., 1983, *Macromolecules*, **16**, 279.
[36] Vorländer, D., 1933, *Trans. Faraday Soc.*, **29**, 907.
[37] Strzelecki, L., and Liébert, L., 1973, *Bull. Soc. Chim. Fr.*, 597, 603 and 605.
[38] Bouligand, Y., Cladis, P. E., Liébert, L., and Strzelecki, L., 1974, *Mol. Cryst. liq. Cryst.*, **25**, 233.
[39] Blumstein, A., Blumstein, R. B., Clough, S. B., and Hsue, C., 1975, *Macromolecules*, **8**, 73.
[40] Eidenschink, R., Erdmann, D., Krause, J., and Pohl, L., 1977, *Angew., Chem. Int. Ed.*, **11**, 633.
[41] Petrzilka, M., 1985, *Mol. Cryst. liq. Cryst.*, **131**, 109.
[42] Schadt, M., Petrzilka, M., Gerber, P. R., and Villiger, A., 1985, *Mol. Cryst. liq. Cryst.*, **122**, 241.
[43] Schadt, M., Buchecker, R., and Müller, K., 1989, *Liq. Crystals*, **5**, 293.
[44] Goto, Y., Ogawa, T., 1988, EPA 0 280 902.
[45] Kelly, S. M., and Fünfschilling, J., 1994, *J. mater. Chem.*, **4**, 1673.
[46] Buchecker, R., unpublished results.
[47] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. Am. Chem. Soc.*, **92**, 1582.
[48] Dewar, M. J. S., and Goldberg, R. S., 1970, *J. org. Chem.*, **35**, 2711.
[49] Gray, G. W., 1981, *Mol. Cryst. liq. Cryst.*, **63**, 3.
[50] Carr, N., Gray, G. W., and Kelly, S., 1981, *Mol. Cryst. liq. Cryst.*, **66**, 267.
[51] Kelly, S. M., Germann, A., Buchecker, R., and Schadt, M., 1994, *Liq. Cryst.*, **16**, 67.
[52] Kelly, S. M., Germann, A., and Schadt, M., 1994, *Liq. Cryst.*, **16**, 491.
[53] Kelly, S. M., 1994, *Liq. Cryst.*, **17**, 211.
[54] Kelly, S. M., Schadt, M., and Seiberle, H., 1995, *Liq. Cryst.*, **18**, 581.
[55] Eidenschink, R., 1983, *Mol. Cryst. liq. Cryst.*, **94**, 119.
[56] Eidenschink, R., Gray, G. W., Toyne, K., and Waechtler, A. E. F., 1988, *Mol. Cryst. liq. Cryst. Lett.*, **5**, 177.
[57] Vorländer, D., 1927, *Z. phys. Chem.*, **A 126**, 449.
[58] Lauk, U. H., Skrabal, P., and Zollinger, H., 1985, *Helv. Chim. Acta*, **68**, 1406.
[59] Kitano, K., Tanaka, M., Goto, Y., and Ogawa, T., 1990, *Mol. Cryst. liq. Cryst.*, **191**, 205.
[60] Seils, F., and Schadt, M., 1995, *Mol. Cryst. liq. Cryst.*, **260**, 127.
[61] Petrzilka, M., Buchecker, R., Lee-Schmiederer, S., Schadt, M., and Germann, A., 1987, *Mol. Cryst. liq. Cryst.*, **148**, 123.
[62] Deutscher, H-J., Laaser, B., Dölling, W., and Zaschke, H., 1978, *J. prakt. Chem.*, **320**, 191.
[63] Kelly, S. M., Buchecker, R., and Schadt, M., 1988, *Liq. Cryst.*, **3**, 1115; 1125.
[64] Kelly, S. M., and Buchecker, R., 1988, *Helv. Chim. Acta*, **71**, 461.
[65] Kelly, S. M., 1989, *Helv. Chim. Acta*, **72**, 594.
[66] Kelly, S. M., 1993, *Liq. Cryst.*, **14**, 675.
[67] Kelly, S. M., and Villiger, A., 1988, *Liq. Cryst.*, **3**, 1173.
[68] Leenhouts, F., Fünfschilling, J., Kelly, S. M., and Buchecker, R., 1989, *Liq. Cryst.*, **5**, 1179.
[69] Kelly, S. M., 1993, *Liq. Cryst.*, **14**, 675.
[70] Fünfschilling, J., Kelly, S. M., and Villiger, A., 1993, *Liq. Cryst.*, **14**, 713.
[71] Kelly, S. M., Fünfschilling, J., and Villiger, A., 1993, *Liq. Cryst.*, **14**, 1169.
[72] Kelly, S. M., Fünfschilling, J., and Villiger, A., 1994, *Liq. Cryst.*, **16**, 813.
[73] Kelly, S. M., and Fünfschilling, J., 1996, *Liq. Cryst.*, **20**, 77.
[74] Kelly, S. M., and Fünfschilling, J., 1996, *Ferroelectrics*, (in the press).
[75] Villiger, A., and Leenhouts, F., 1991, *Mol. Cryst. liq. Cryst.*, **209**, 297.
[76] Kelly, S. M., 1984, *Helv. Chim. Acta*, **67**, 1572.
[77] Schad, H., and Kelly, S. M., 1984, *J. Chem. Phys.*, **81**, 1514.
[78] Buchecker, R., and Schadt, M., 1992, EPA, 0 464 648 A1.
[79] Kelly, S. M., and Schadt, M., 1994, CH 2067/94.
[80] Kelly, S. M., and Fünfschilling, J., 1993, *J. mater. Chem.*, **3**, 953.
[81] Kelly, S. M., Buckecker, R., and Fünfschilling, J., 1994, *J. mater. Chem.*, **4**, 1689.
[82] Kelly, S. M. and Fünfschilling, J., 1994, *J. mater. Chem.*, **4**, 1673.
[83] Kelly, S. M., and Fünfschilling, J., 1995, *J. mater. Chem.*, **5**, 1335.
[84] McMillan, W. W., 1973, *Phys. Rev. A*, **8**, 1921.
[85] Wulf, A., 1975, *Phys. Rev. A*, **11**, 365.
[86] Priest, R. G., 1976, *J. chem. Phys.*, **65**, 408.
[87] Praefke, K., Schmidt, D., and Heppke, G., 1990, *Chem. Ztg.*, **104**, 269.
[88] Goto, Y., Ogawa, T., 1988, EPA 0 280 902.
[89] Goto, Y., Ogawa, T., Sawada, S., and Sugimori, S., 1991, *Mol. Cryst. liq. Cryst.*, **191**, 209.
[90] Kelly, S. M., Fünfschilling, J., and Leenhouts, F., 1991, *Liq. Cryst.*, **10**, 243.
[91] Fujita, A., Goto, Y., and Nakagawa, E., 1994, *Liq. Cryst.*, **5**, 707.
[92] Kelly, S. M., 1991, *Mol. Cryst. liq. Cryst.*, **204**, 27.
[93] Kelly, S. M., 1991, *Liq. Cryst.*, **10**, 261; 273.
[94] Kelly, S. M., Schadt, M., and Seiberle, H., 1992, *Liq. Cryst.*, **11**, 761.

[95] Sato, H., Furukawa, K., and Sugimori, S., 1979, EPA 0 002 136.

[96] Osman, M. A., and Revesz, L., 1982, *Mol. Cryst. liq. Cryst. Lett.*, **82,** 41.

[97] Takeuchi, K., Tanaka, Y., and Takatsu, H., 1993, in *Preprints of the 20th Japanese Liquid Crystals Meeting*, p. 66.

[98] Bezborodov, V. A., Konovalov, V. A., Lapanik, V. I., and Min'ko, A. A., 1989, *Liq. Cryst.*, **4,** 209.

[99] North, B. E., Shipley, G. G., and Small, D. M., 1976, *Biochim. Biophys. Acta*, **424,** 376.

[100] Pohlmann, L. W., Elser, W., and Boyd, P. R., 1971, *Mol. Cryst. liq. Cryst.*, **13,** 243.

[101] Elser, W., 1976, *Advances in Liquid Crystals*, Vol. 2, edited by G.H. Brown (New York: Academic Press), p. 73 and references therein.

[102] Ennulat, R. D., 1969, *Mol. Cryst. liq. Cryst.*, **8,** 247.

[103] Zhong, L., Fung, B. M., Twieg, R., Betterton, K., Walba, D. M., Shoa, R. F., and Clark, N. A., 1991, *Mol. Cryst. liq. Cryst.*, **199,** 379.