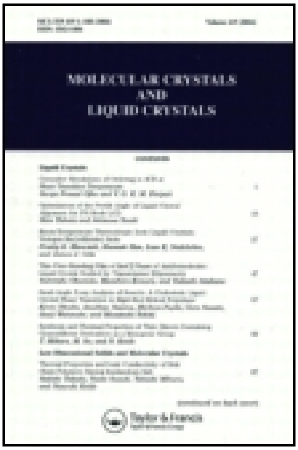

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Near-UV Transparent Nematics

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NEAR-UV TRANSPARENT NEMATICS

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UV-transparent nematic liquid crystals synthesised specifically for use as components of nematic mixtures for the Photoluminescent Liquid Crystal Display (PL-LCD) are reported. These polar and apolar nematic liquid crystals do not possess conjugated phenyl rings or cyano-groups. Where two phenyl rings are present, they are separated by a non-conjugated linking group, so that they do not absorb in the visible or the near ultra-violet. Polar and apolar nematics have been combined to generate UV-transparent nematic mixtures of positive dielectric anisotropy for use in TN-PL-LCDs and STN-PL-LCDs transmitting monochromatic UV light at 365 or 390 nm.

Keywords: near UV transparent; nematics; PL-LCDs

INTRODUCTION

The Photoluminescent Liquid Crystal Display (PL-LCD) [1,2] uses an LCD to modulate near UV light from a flat UV lamp incident on a phosphor screen. This has the advantage of decoupling the modulated light from the emitted light, which is Lambertian. The optics of the TN-LCD [3,4] or STN-LCD [5–8] used can be optimised for one wavelength and one transmission angle. This has the further advantage of optimising the electro-optic response of the LCD. However, the PL-LCD requires a UV-transparent

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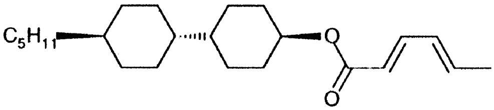
*Corresponding author. E-mail: S.M.Kelly@hull.ac.uk nematic mixture with the desired characteristics for either of these displays. A suitable commercial nematic mixture has not been identified so far. We report the synthesis of some new and some known [9,10] nematic liquid crystals to be used as components of such nematic mixtures. Suitable single components were not available from commercial suppliers of liquid crystals for this investigation of UV-transparent liquid crystals.

The UV spectra of organic compounds are the result of transitions between electronic energy levels such as those between a bonding or lone-pair orbital and an unfilled non-bonding or antibonding orbital. Transitions from excited σ-bonds (e.g., -CH_2-CH_2-) give rise to absorption between 120 nm and 200 nm in the UV. Transitions such as n-π^* and π-π^* of heteroatoms (e.g., -CH_2O-), ketones (C=O) or carbon-carbon double bonds (C=C) also absorb below 200 nm. Although n-π^* transitions of the carbonyl group of ketones absorb at 300 nm, this transition is forbidden and the probability of this transition is very low (molar coefficient of absorption, $\varepsilon_{max} = 100$; cf. $\varepsilon_{max} = 10{,}000$ for fully allowed transitions). Even conjugated open-chain dienes with two carbon-carbon double bonds absorb at relatively short wavelengths (<250 nm). Thus, the nematic liquid crystal shown [11] below with a core of two *trans*-1,4-disubstituted cyclohexane rings (Cr-N = 117°C; N-I = 180°C), an α,β-unsaturated carboxy group and two conjugated carbon-carbon double bonds still exhibits no absorption at all above 300 nm including forbidden transitions (λ_{max} = 260 nm). This is less than the wavelength of the monochromatic UV light (365 nm) used in PL-LCD.

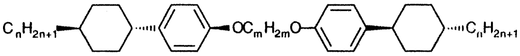


We report the synthesis of a range of nematic liquid crystals with very little absorption at 365 nm. The molecular structure of these new chemical entities are constituted from components, such as *trans*-1,4-disubstituted cyclohexane rings and heteroatoms (O, F). These liquid crystals can be used to prepare nematic mixtures suitable for TN-LCDs and STN-LCDs.

SYNTHESIS

The ethers **1–20** shown in the Tables 1 and 2 were prepared by a Williamson alkylation reaction of α,ω-dibromoalkanes and *trans*-4-(4-propylcyclohexyl)phenol and *trans*-4-(4-pentylcyclohexyl)phenol. The ethers (**21** and **22**) were prepared by a Williamson alkylation reaction between the sodium salt of *trans*-4-(*trans*-4-*n*-alkylcyclohexyl)cyclohexanol and methyl iodide. The ethers **23–30** were synthesised in a Williamson alkylation

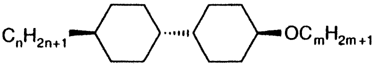
TABLE 1 Transition Temperatures (°C) for the Dimers (**1–20**)



	n	m	Cr		SmC		N		I
(**1**)	3	3	●	86		–		–	●
(**2**)	3	4	●	174		–	(●	164)	●
(**3**)	3	5	●	99		–		–	●
(**4**)	3	6	●	128		–	●	146	●
(**5**)	3	7	●	84		–	(●	77)	●
(**6**)	3	8	●	105		–	●	132	●
(**7**)	3	9	●	88		–	●	96	●
(**8**)	3	10	●	106		–	●	120	●
(**9**)	3	11	●	92		–	●	97	●
(**10**)	3	12	●	108		–	●	113	●
(**11**)	5	3	●	86		–		–	●
(**12**)	5	4	●	155	●	160	●	166	●
(**13**)	5	5	●	95		–	●	98	●
(**14**)	5	6	●	117	●	134	●	146	●
(**15**)	5	7	●	85		–	●	98	●
(**16**)	5	8	●	106	●	108	●	129	●
(**17**)	5	9	●	83		–	●	97	●
(**18**)	5	10	●	97	●	99	●	121	●
(**19**)	5	11	●	88		–	●	101	●
(**20**)	5	12	●	109		–	●	114	●

reaction between *trans*-4-(4-propylcyclohexyl)phenol and *trans*-4-(4-pentylcyclohexyl)phenol and commercially available benzyl bromides. The corresponding dimethylene-linked compounds were prepared by two methods. In the first method a Grignard reaction using commercially available benzyl bromides and *trans*-4-(4-pentylcyclohexyl)benzonitrile

TABLE 2 Transition Temperatures (°C) for the *trans*,*trans*-4-*n*-alkyl–4′-*n*-alkoxy-1,1′-bicyclohexanes (**21**, **22**)



	n	m	Cr		SmB		N		I
(**21**)	3	1	●	10	–		●	17	●
(**22**)	5	1	●	12	●	29	●	36	●

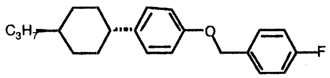
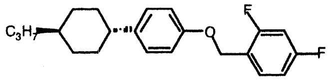
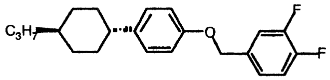
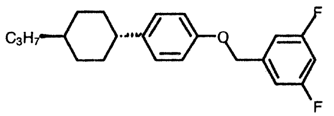
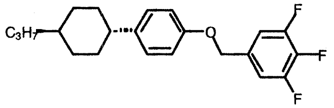
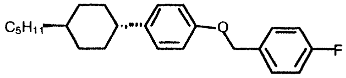
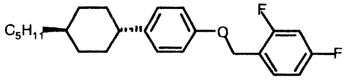
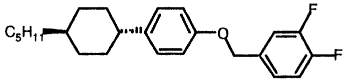
(PCH5) yielded a ketone, which was reduced by catalytic reduction using palladium on charcoal. In the second method the nitrile was converted to the corresponding aldehyde using DIBAL, which was converted to a stilbene by a Wittig reaction with the Wittig reagent formed in the normal way from triphenyl phosphine and benzyl bromides. The stilbene was then hydrogenated using palladium on charcoal to yield the desired compound with a saturated dimethylene linkage between the two phenyl rings.

RESULTS AND DISCUSSION

1. Transition Temperatures

The structures and transition temperatures of the dimers **1–20** are collated in Table 1. The alternation (odd-even effect) in the nematic clearing point shown by the two homologous series (**1**–**10** and **11**–**20**) is a well-known phenomenon and has been attributed to the lower length-to-breadth ratio of the homologues with an odd number of methylene units (CH_2) in the central spacer compared to that of those homologues with an even number of methylene units (CH_2) in the central spacer. The former exhibit a bent conformation, whereas the latter possess a linear conformation assuming an all-*trans*, antiperiplanar conformation of the spacer. There is usually a direct correlation between the magnitude of the nematic clearing point and the geometric length to breadth ratio and the resultant anisotropy of polarisability. The presence of an enantiotropic smectic C phase for the homologues (**12**, **14**, **16** and **18**) with an even number of methylene units in the central linkage can also be explained by the linear geometrical shape. The compounds collated in Tables 3 and 4 illustrate the effect of fluorine substituents in terminal and lateral positions in nematic liquid crystals. The difluoro-substituted, trifluoro-substituted and 4-trifluoromethoxy-substituted materials (**25**, **27**, **30**–**33**) exhibit very low melting points for three-ring compounds. The melting point of the mono-fluoro-, 3,4-difluoro- and 3,4,5-trifluoro-substituted ethers (**23**, **25** and **27**) decreases with increasing degree of substitution. This lowers the van der Waals forces of attraction. The 3,4-difluoro-substituted ethers (**25** and **30**) exhibit a nematic phase, whereas the trifluoro-substituted ether (**27**) does not possess an observable nematic phase. Both of these phenomena can be attributed to steric effects as the presence of the fluorine atom in position 3 and 5 lead to a broadening of the molecular rotation volume. The chiral dopants (**34**–**37**) are all liquids probably due to the steric effects of the branched terminal chains and the presence of only two rings in the molecular core.

TABLE 3 Transition Temperatures (℃) for the Ethers (**23–30**)

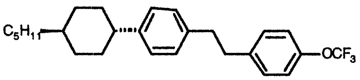
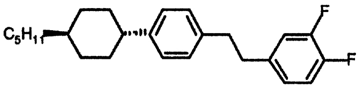
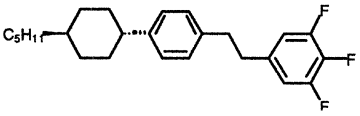
		Cr		N		I
(**23**)		●	124		–	●
(**24**)		●	88		–	●
(**25**)		●	74	(●	52)	●
(**26**)		●	72		–	●
(**27**)		●	68		–	●
(**28**)		●	100	(●	74)	●
(**29**)		●	82		–	●
(**30**)		●	59	●	69	●

( ) Represents a monotropic transition temperature.

2. Mixtures

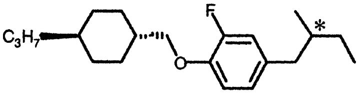
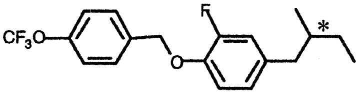
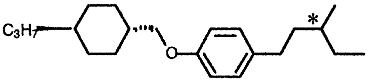
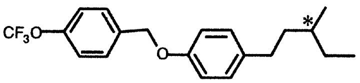
Selected homologues of the dimers (**1–20**) are used in combination with a binary mixture of the known ethers (**21** and **22**) to form host nematic mixtures of neutral dielectric anisotropy. The ethers (**21** and **22**) form a UV-transparent nematic phase at room temperature, whose clearing point is increased by the addition of small amounts of the dimers. The difluoro-substituted, trifluoro-substituted and 4-trifluoro-methoxy substituted

TABLE 4 Transition Temperatures (°C) for the Ethers (**31–33**)

		Cr		SmB		N		I
(**31**)		●	68	●	47	●	74	●
(**32**)		●	43		–	(●	31)	●
(**33**)		●	21		–	(●	19)	●

materials (**25**, **27**, **30**–**33**) exhibit low melting points and relatively high dielectric anisotropy. Therefore, they can be added to the neutral host nematic mixture to form a resultant nematic mixture of positive dielectric anisotropy. Such poly-fluorinated nematic liquid crystals with no adjacent

TABLE 5 Structures, Melting Points (°C) and Helical Twisting Powers, Determined in Merck Nematic Mixture MLC 9000, for the Chiral Dopants (**34**–**37**)

		Cr		I	HTP
(**34**)		●	<25	●	8.8 μm^{-1}
(**35**)		●	<25	●	6.1 μm^{-1}
(**36**)		●	<25	●	
(**37**)		●	<25	●	

*Represents an optically active chiral centre.

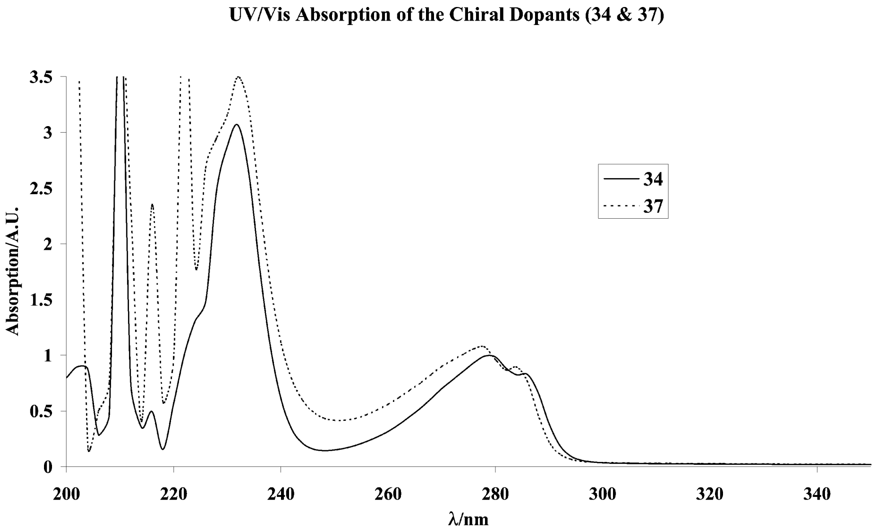


FIGURE 1 UV/V is absorption of the chiral dopants (34 & 37).

phenyl rings are required as our studies have confirmed that compounds containing two conjugated phenyl rings, such as 4-*n*-alkyl-4′-cyanobiphenyls, are not sufficiently stable for use in PL-LCDs [12]. The chiral dopants (**34**–**37**) exhibit a high helical twisting power, see Table 5, and were used to dope these nematic mixtures in order to generate chiral nematic mixtures with an appropriate degree of twist for use in PL-LCDs with TN-LCDs and STN-LCDs as the beam modulator [12]. All of the compounds (**1**-**37**), whose UV spectra were measured in solution, do not absorb above 340 nm. Therefore, they are transparent at the wavelengths of UV light (365 and 390 nm) used in prototype PL-LCDs, see Figure 1 for a typical UV-vis spectrum of the chiral dopants (**34** and **37**). Therefore, the compounds (**1**–**37**) reported here are suitable components of nematic mixtures for use in prototype PL-LCDs. The properties of some of these mixtures has been evaluated and found to be stable under UV illumination [12].

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