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Structure-property correlations of new materials comprising of a cyclic enone for TFT-LCD applications

Louise D. Farrand[a][b]; Y. Utsumi[a]; H. Kagawa[a]; K. Kondo[a]
[a] Hitachi Research Laboratory, Hitachi Ltd., Ibaraki-ken, Japan [b] Merck Ltd., Poole, England

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Structure–property correlations of new materials comprising of a cyclic enone for TFT-LCD applications

by LOUISE D. FARRAND*†, Y. UTSUMI, H. KAGAWA and K. KONDO
Hitachi Research Laboratory, Hitachi Ltd., 1-1. Omika-cho 7 chome, Hitachi-shi, Ibaraki-ken, 319-12 Japan

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Dielectric, birefringence and voltage–transmission characteristics of novel cyclic enone compounds are reported. The new materials are shown to exhibit high dielectric anisotropies and modest refractive index anisotropies. These results are explained by structural and substituent effects and are in accordance with the results expected from molecular modelling. The analogy found between structural and physical properties may be used to design improved materials for TFT-LCDs. The use of cyclic enones as dopants to contribute to a reduction in the threshold voltage of liquid crystal mixtures for TFT-LCDs is foreseeable.

1. Introduction

Thin film transistor liquid crystal displays (TFT-LCDs) combine the reliability offered by the twisted nematic effect [1] with semiconductors to offer a high performance actively addressed device which can display a large amount of information. These displays are now used in many applications such as portable computers, car navigation systems and televisions [2]. One reason that currently available TFT-LCDs are expensive to manufacture is due to the high cost of the driving schemes [3]. To use cheaper driving schemes, the threshold voltage must be lowered. Another reason to lower the threshold voltage is that the display power consumption will be lowered and would therefore permit a remote user to operate a portable display for a greater length of time.

Materials which combine high dielectric ($\Delta\varepsilon$) and low refractive index anisotropies (Δn) are desirable for TFT-LCDs. Recently, almost all new compounds reported as dopants for TFT-LCD mixtures, for the purpose of introducing high $\Delta\varepsilon$ without a corresponding increase in Δn, are based on arylcyclohexyl systems substituted with fluorine atoms to introduce polarity into the molecules [4, 5].

In this paper, we report some physical properties of a new, stable class of compounds based on the cyclic enone ring structure [6] shown in figure 1.

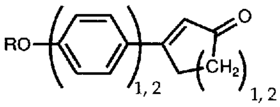
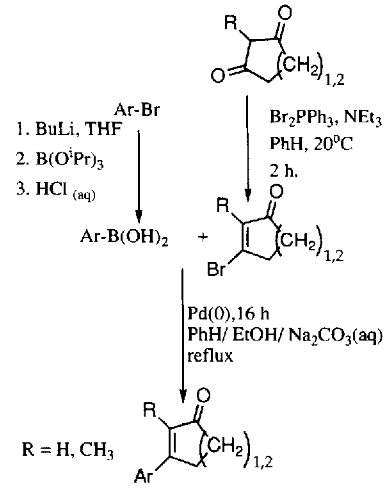


Figure 1. Arylcyclic enone structure.



Scheme. Preparation of arylcycloalkenones.

The enone which is incorporated into the rigid molecular core behaves as a strongly polar terminal group. Although the compounds reported in this paper were originally designed as intermediates for new materials for other applications [7], we anticipated that the electronic properties of the enone structure would also make these materials useful for TN devices [8]. Therefore, we measured some physical properties of the cyclic enones with the expectation that these compounds may be suitable high $\Delta\varepsilon$ additives for the purpose of reducing the threshold voltage in materials for TFT-LCDs.

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*Author for correspondence.

†Present address: Merck Ltd., West Quay Road, Poole, BH15 1HX, England.

2. Experimental

A detailed synthetic procedure is described elsewhere [9]. The synthetic procedure is outlined in the scheme. The 3-aryl-2-cycloalkenones were prepared in near quantitative yields from the palladium(0) sp^2 cross-coupling reaction of 3-bromo-2-en-1-ones with an appropriate arylboronic acid.

MOPAC [10] was used to determine the overall dipole moment contribution in the direction of the long molecular axis for the two ring systems. The transition temperatures were determined by thermal light microscopy using a Zeiss Universal microscope equipped with crossed polarizers and a Linkam hot stage with an integrated temperature controller. $\Delta\varepsilon$ and Δn measurements were made using approximately 10 wt % of dopant in ZLI-4792 (Merck). The single cell method [11] was used to determine the temperature dependence of $\Delta\varepsilon$ in the mixtures. The cell gap was 25 μm, the surfaces were rubbed anti-parallel and the ITO electrodes were 15 mm in diameter. The temperature and wavelength dependent birefringence measurements were made using an Olympus AH2-SRK/STK spectroscopic microscope in anti-parallel rubbed cells. The cell gaps were determined by the interferometric method [12] and were typically 20 μm. Δn values were compared at 550 nm. The voltage–transmission characteristics were recorded in a positive contrast TN cell with a 5·33 μm gap at zero viewing angle and at 25°C.

3. Results and discussion

3.1. *Melting points and T_{NI} data*

The 2-ringed cyclohexenones (**1** and **2**) and cyclopentenones (**3**, **4** and **5**) are not mesogenic. The 3-ringed biarylcyclopentenone (**6**) exhibits a low temperature nematic phase.

The melting points (m.p.) of the cyclic enones reflect the effect of structural features of the molecules on the ordering and packing of the compounds in the solid state. From the m.p. data in table 1, it can be seen in the cyclopentenones (**3**, **4** and **5**) that the methyl group decreases the melting point by disrupting the packing of the molecules. However, in the cyclohexenones (**1** and **2**), the methyl group only adds to the molecular bulk and increases the m.p. T_{NI} data (10 wt %) of enone in host are given. At 20 wt %, the cyclic enones unsubstituted at the sp^2 carbon (**1** and **3**) were insoluble and the methyl substituted systems (**2**, **4** and **5**) had very low T_{NI} values. It is likely that the methyl group prevents the close packing of molecules and so the methylated compounds are more likely to behave as pseudo-nematic compounds rather than smectic compounds. Without the methyl group, the cyclic pentenones could easily form a layered structure. The high tendency for nematic behaviour can be observed in compound **6**, which possesses a long alkoxy chain. Long chains often lead to the formation of smectic phases, however for this compound only a nematic mesophase is observed.

3.2. *Dielectric anisotropy*

3.2.1. *Temperature dependence*

$\Delta\varepsilon$ temperature dependence measurements of the enones in host ZLI-4792 are shown in figure 2.

At all values of T-T_{NI}, all of the doped mixtures show an increase in $\Delta\varepsilon$ compared with the host material. To evaluate the effect of an equivalent number of moles of each dopant in the mixture, the data presented in table 2 are given as equimolar percent of enone in the host.

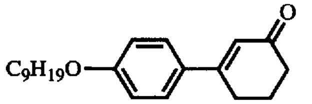
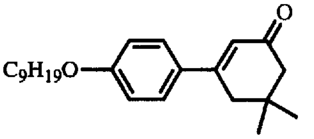
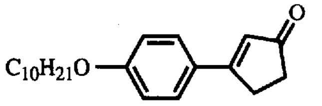
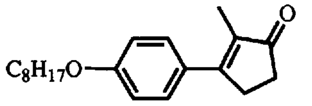
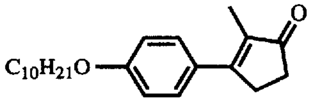
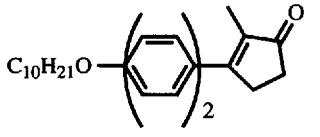
Haller plots were obtained. At absolute zero there is no orientational disorder and so the potential of the enone derivatives as dopants could be assessed. The relative sizes of $\Delta\varepsilon$ at 0 K were consistent with the order of values at $T-T_{NI}=-40$°C, i.e. **4** had the largest value and **1** the smallest. All of the doped mixtures possessed a larger $\Delta\varepsilon$ than the host. The Haller plot of doped mixture **4** and the host is shown in figure 3 as a typical example.

3.2.2. *Structural analysis of $\Delta\varepsilon$ data*

The cyclopentenones possess higher dielectric anisotropies ($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$) than the cyclohexenones. Molecular modelling [13] shows that this result may be attributed to the shape of the two ring systems and the relative positions of the ketone group with respect to the long molecular axis. From molecular modelling [13], see figure 4, the enone in the 5-membered ring is shown to lie more parallel to the long molecular axis than the enone of the 6-membered rings which occupies a slightly more lateral position. The cyclopentenone is shown to have a larger dipole contribution [10] along the principal inertia axis.

A comparison of the two cyclohexenones (**1** and **2**) shows that substitution at the 5,5-position with two methyl groups increases $\Delta\varepsilon$. The placement of a methyl at the 2-position of the cyclopentenone (see **3**, **4** and **5**) also results in an increase in $\Delta\varepsilon$. The positive inductive effect [14] of the methyl group at the 2-position will donate electrons into the delocalized enone part of the ring causing the permanent dipole to increase mainly along the long molecular axis: a larger $\Delta\varepsilon$ results. It should be possible to further increase $\Delta\varepsilon$ in compounds **1** and **2** by placing a methyl group at the 2-position where it may have a larger effect, rather than at the more insulating 5-position. The biaryl cyclic enone (**6**) possesses a smaller $\Delta\varepsilon$ than the 2-ringed cyclopentenone compounds. The lower value may be due to a dilution effect of the larger size of the 3-ringed molecule compared to the enone.

Table 1. M.p. and T_{NI} data of enones in ZLI-4792.

Compound	Structure	m.p.	$T_{NI} \approx 10$ wt %
ZLI-4792		N 93·2 I	
1		Cr 51 I	78·5
2		Cr 63 I	63·5
3		Cr 59 I	79·5
4		Cr 37 I	69·5
5		oil	72·5
6		Cr 63 N 68 I	89·2

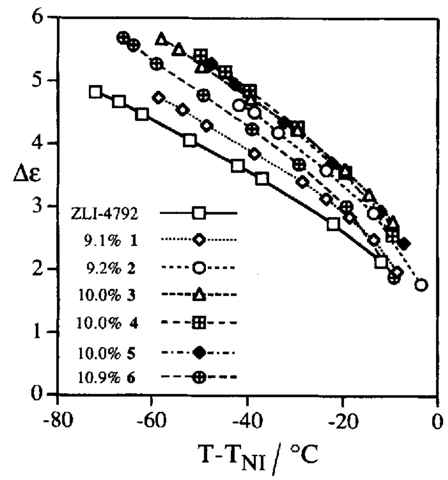


Figure 2. Measurements results of Δε versus $T-T_{NI}$ of wt % dopants in ZLI-4792.

Table 2. Dielectric anisotropy measurements for $1{\cdot}0 \times 10^{-3}$ mol g^{-1} of enone in ZLI-4792 at T-$T_{NI} = -40°$ and $-20°C$. The 0 K values are extrapolated.

Compound	$1{\cdot}0 \times 10^{-3}$ mol g^{-1} of enone in host		Extrapolated value of 0 K.
	T-$T_{NI} = -40°C$	T-$T_{NI} = -20°C$	
ZLI-4792	3·57	2·63	7·16
1	4·06	2·97	7·20
2	5·18	3·35	7·60
3	5·21	3·48	8·04
4	5·51	3·65	8·64
5	5·40	3·55	8·16
6	4·70	3·08	8·00

3.3. *Birefringence*

3.3.1. *Temperature dependence*

Δ*n* temperature dependence measurements of the enones in host ZLI-4792 are shown in figure 5, and results for the $1{\cdot}0 \times 10^{-3}$ mol g^{-1} of enone in host material are given in table 3.

At $T-T_{NI} = -40°C$, the doped mixtures have an equal (compound **1**) or slightly larger Δ*n* than the host material. These optical anisotropy temperature dependence data are different from the dielectric anisotropy

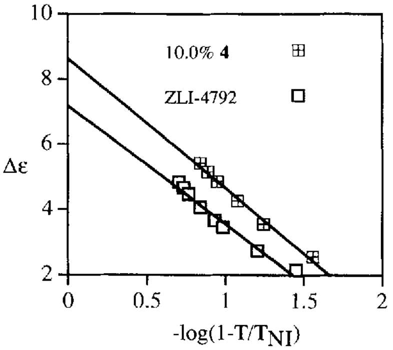


Figure 3. Haller plots of mixture **4** and ZLI-4792.

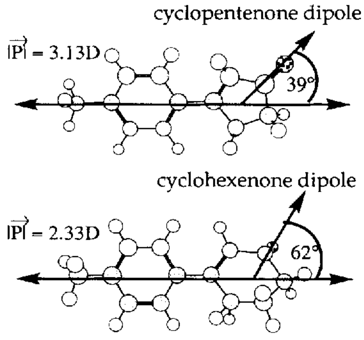


Figure 4. 3D modelling of the arylcyclopentenone and arylcyclohexenone structures.

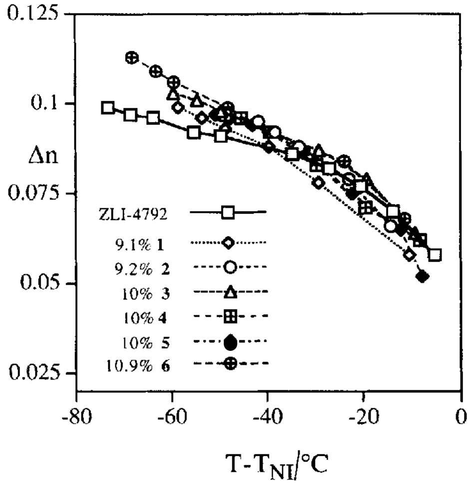


Figure 5. Measurements results of Δn versus $T-T_{NI}$ of wt % dopants in ZLI-4792.

data. The mixtures doped with enones show a moderate increase in birefringence but a large increase in $\Delta\varepsilon$.

3.3.2. *Structural analysis of Δn data*

Cyclohexenone mixture (**1**) has a low birefringence (0·088) at $T-T_{NI}=-40$°C. The effect of the two methyl substituents on this ring structure is to substantially increase this value (see table 3). Modelling shows that methyl groups at the 5,5-position of an arylcyclohexenone are directed along the long molecular axis and since $\Delta n = n_e - n_o$, where n_e is the extraordinary refractive index and n_o the ordinary refractive index; the methyl groups increase the n_e component and hence increase birefringence. On the other hand, methyl substitution at the sp^2 carbon of the cyclopentenone (**4** and **5**) has the opposite effect. In this case, the optical anisotropy is lowered. At the sp^2 position, the methyl group is perpendicular to the main molecular axis: this serves to increase n_o and reduces Δn.

Table 3. Birefringence measurements for $1\cdot0 \times 10^{-3}$ mol g^{-1} of enone in ZLI-4792 at $T-T_{NI}=-40$° and -20°C.

	$1\cdot0 \times 10^{-3}$ mol g^{-1} of enone in host	
Compound	$T-T_{NI}=-40$°C	$T-T_{NI}=-20$°C
ZLI-4792	0·088	0·077
1	0·088	0·061
2	0·097	0·075
3	0·096	0·080
4	0·093	0·072
5	0·093	0·072
6	0·101	0·076

The refractive indices of organic materials are largely dependent on the degree of π conjugation in the molecular structure. Molecular modelling in figure 4 shows that the π electrons of the arylcyclopentenones contribute more to the polarizability along the long molecular axis than in the arylcyclohexenones. The result is that the arylcyclopentenones have a higher birefringence because n_e is larger. This effect can be observed by comparing compounds **1** and **3**. Compound **5** has a high refractive index anisotropy: this is caused by the high degree of conjugation in the rigid core.

3.4. *Voltage–transmission characteristics*

The threshold voltage of 10 wt % (**5**) in ZLI-3788 was measured and the data was compared with that of the host mixture. The plot of relative transmittance (per cent) versus voltage is shown in figure 6 and the data at 10, 50 and 90 per cent brightness are given in table 4. The threshold voltage of the arylcyclopentenone doped mixture is significantly reduced compared to that of the basic mixture.

5. Conclusions

The purpose of this work was to study the structure–property relationships of a new class of materials. The study also investigated if the cyclic enone structure could be used as a suitable additive for TFT-LCD mixtures for the purpose of reducing the threshold voltage. The

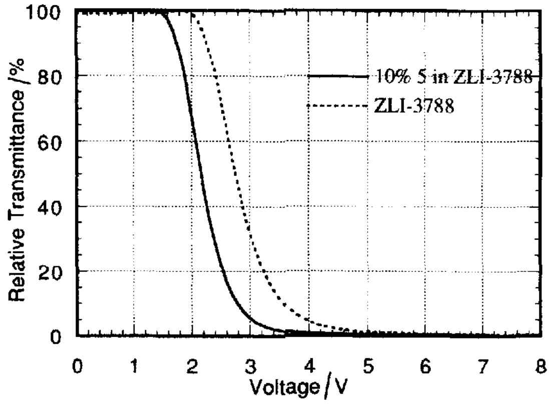


Figure 6. Plot of relative transmission versus voltage of compound **5** (10 wt %) and ZLI-3788 in a TN cell.

Table 4.

ZLI-3788	10 per cent **5** in ZLI-3788
$V(90, 0, 25)=2{\cdot}28$ V	$V(90, 0, 25)=1{\cdot}76$ V
$V(50, 0, 25)=2{\cdot}76$ V	$V(50, 0, 25)=2{\cdot}17$ V
$V(10, 0, 25)=3{\cdot}58$ V	$V(10, 0, 25)=2{\cdot}79$ V

cyclic enones possess a high positive $\Delta\varepsilon$, which is a desirable property in mixtures for TFT-LCDs. The arylcyclopentenones have larger dielectric anisotropies than the arylcyclohexenones. The permanent dipole moment can be enhanced by substitution of a positive inductive group (methyl) at an appropriate position. Moreover, lateral substitution of a methyl group was shown to decrease Δn at the same time it increased $\Delta\varepsilon$. This relationship could be extended to other materials designed for TFT-LCD mixtures. As anticipated, the high dielectric anisotropic property of compound **5** caused a considerable decrease in the threshold voltage compared to that of a host material.

This study focused only on the structure–property relationships of the cyclic enone structure. The overall molecular structure can be improved for TFT-LCD applications. We are now optimizing these structures by replacing the phenyl ring with cyclohexane to reduce birefringence, and using shorter alkyl terminal groups to improve compatibility with the nematic host materials. We are investigating the substitution of fluorine atoms at the 5-position of the cyclopentenones for the purpose of increasing the dielectric anisotropy.

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