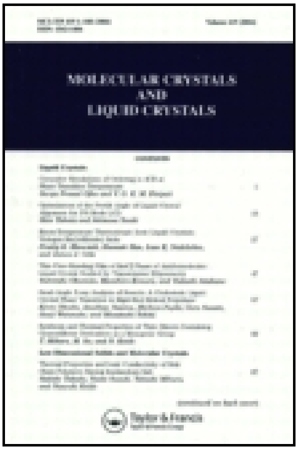

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The Properties of Bicyclo[2.2.2]Octane Esters†

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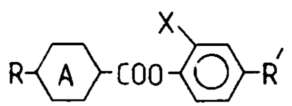
The physical properties of three types of ester containing the bicyclo[2.2.2]octane ring are reported and compared with analogous esters based on benzene and cyclohexane rings. The electro-optic properties in twisted nematic displays of mixtures of these esters with cyanobiphenyls and PCH materials are also reported. These show that mixtures based on the bicyclo[2.2.2]octane esters have particularly low temperature dependencies and are therefore better suited for use in multiplexed displays than esters based on benzene and cyclohexane rings.

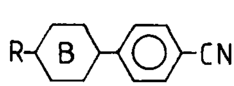
INTRODUCTION

Three homologous series of esters, with wide nematic ranges, (structure I, with A = bicyclo[2.2.2]octane [BCO] ring and X = hydrogen or fluorine)



(I)

have recently been synthesized by Gray and Kelly.[1] The analogous cyclohexane esters (A = cyclohexane ring and X = hydrogen) and benzoate esters (A = benzene ring and X = hydrogen) are already widely used in conjunction with cyanobiphenyls (B = benzene ring) and PCH's (B = cyclohexane ring) of structure II as components of multiplexing mixtures for twisted nematic display devices, and in this paper we compare the new



(II)

† Presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

BCO esters with these more familiar esters. Such mixtures of esters (I) and cyano compounds (II) show improved threshold steepness and lower temperature dependence of threshold voltage when compared with mixtures composed solely of cyano compounds (II), and are therefore particularly useful in multiplexed displays.

The basic physical properties of the pure BCO esters have been measured using the compounds and mixtures shown in Table I. In two cases approximate eutectic mixtures were used which gave good depression of melting point, enabling measurements to be made over a wide range of temperatures; equivalent end groups were used.

The BCO esters were then doped slightly positive ($\Delta\epsilon \approx +2$), to enable their electro-optic properties to be measured, and finally they were incorporated and assessed in low voltage multiplexing mixtures ($\Delta\epsilon \approx +10$).

Physical properties of the pure esters

The basic physical properties of the three types of BCO ester were measured and are compared in Table II with those of the more familiar benzoate and cyclohexane esters and the recently synthesized fluoro-substituted cyclohexane esters[2] (structure I, with A = cyclohexane ring and X = fluorine).

The bulk viscosities were measured as a function of temperature (Figure 1) using a rotating cone viscometer, with the temperature controlled to within 1°C. It is interesting to note that the viscosities of the BCO esters at 20° C ($\bar{\eta}$ = 30–60 cP) are comparable with those of other esters. Making B a BCO ring in the cyano compounds (II) significantly increases the viscosity ($\bar{\eta} \approx$ 100 cP at

TABLE I

Nematic ranges of the BCO ester mixtures and compounds used

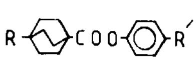
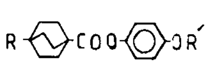
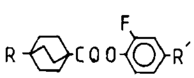
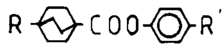
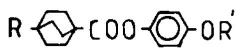
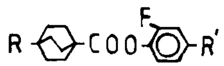
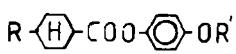
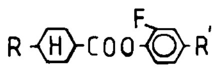
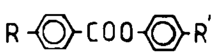
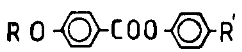
Ester	R	R′	Nematic Range (°C)	Mixture or compound used	Nematic Range of mixture, compound (°C)
	C_3H_7	C_5H_{11}	29.5 → 55.5	50 : 50	≈ 5 → 58
	C_5H_{11}	C_5H_{11}	30 → 61.5		
	C_3H_7	C_4H_9	40 → 92	50 : 50	≈20 → 94
	C_5H_{11}	C_4H_9	42 → 100		
	C_5H_{11}	C_5H_{11}	26 → 65	5/5	26 → 65

TABLE II

Properties of esters measured at 20°C

Ester	Typical T_{NI} (°C)	Viscosity (cP)	Δn	$\Delta\epsilon$
	60	34	0.075	−0.61
	95	64	0.088	−1.34
	60	44	0.076	−0.95
	40	18	0.07	−0.5
	70	44	0.08	−1.4
	35	22	0.07	−0.8
	20	23*	0.13*	+0.4*
	50	65	0.14	+0.1

* Extrapolated values

20° C).[3] We suggest that in structure II the ester linkage masks the effect on viscosity of the bulky BCO ring.

The refractive indices were measured using an Abbé refractometer operating at the sodium D line (589 nm). By homeotropically aligning the prisms with lecithin both n_e and n_o were measured simultaneously. The optical birefringence of the BCO esters is low ($\Delta n \approx 0.08$) and comparable with those esters where A = cyclohexane ring.

The dielectric constants were calculated from capacitance measurements made in a moderate magnetic field (0.5 to 1.5 T), followed by extrapolation to infinite magnetic field.[4]

Twisted nematic electro-optic properties of mixtures with low dielectric anisotropy

The BCO esters were doped weakly positive ($\Delta\epsilon \approx +2$) by adding 2CB (a cyanobiphenyl with R = C_2H_5) which has a high positive dielectric aniso-

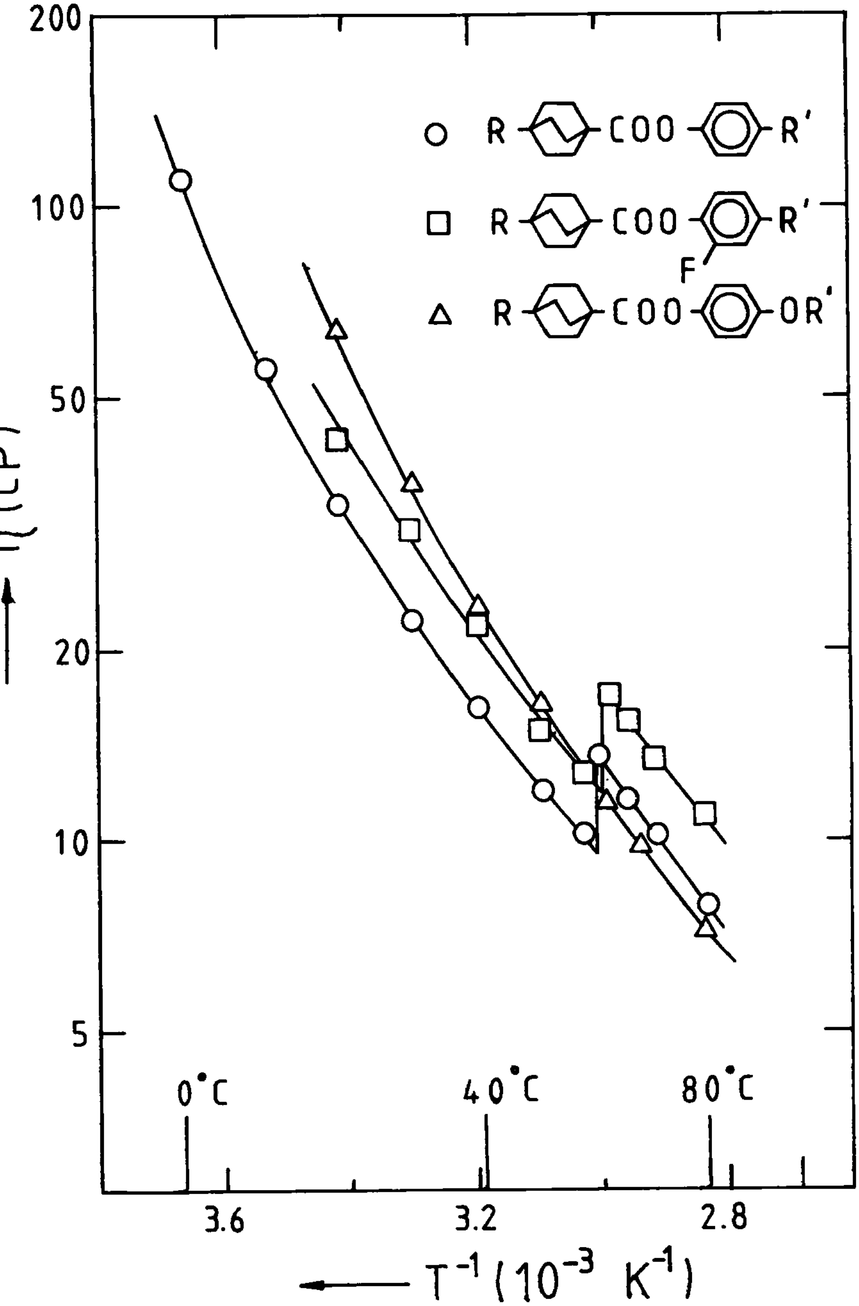


FIGURE 1 Bulk viscosities of the BCO esters.

tropy and is extremely efficient at depressing smectic phases. These mixtures were assessed in transmission using a previously described experimental technique and nomenclature[5] summarized below. These mixtures have low birefringence ($\Delta n \approx 0.09$) and were therefore assessed using 12 μm thick twisted nematic cells to ensure good guiding of the plane of polarization. The cells had a low tilt alignment (rubbed PVA) and an accurately defined twist angle of 90° ±1°, and were examined between exactly crossed polars using a 100 Hz sq wave drive signal. The materials measured contained no cholesteric additive, the "correct" twist being induced by application of about 20 V for a few minutes. The measurements at 10° and 45° to the normal were made looking into the quadrant with the lowest threshold voltage at grazing incidence.

The voltages, V, are defined in terms of X, θ and T:

$$V_X(\theta, T)$$

where

X = % transmission. This is normalized to 100% when V = 0.
θ = angle of measuring beam from normal incidence
T = measurement temperature
V_c = threshold voltage = $V_{90}(45°, T)$

$$\text{Temperature dependence} = -\frac{1}{V_c}\left(\frac{dV_c}{dT}\right)$$

$$M_{20} = V_{10}(0°, 20°C)/V_{90}(45°, 20°C)$$

$$M'_{20} = V_{50}(10°, 20°C)/V_{90}(45°, 20°C)$$

The temperature dependence of V_c and the electro-optic steepness M_{20} and M'_{20} together with some other properties of the BCO ester mixtures are given in Table III. Table IV compares the temperature dependence and M'_{20} with values typical for mixtures containing other types of ester.

TABLE III

Electro-optic properties of mixtures containing 10% 2 CB measured at 20°C

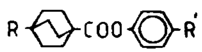
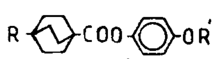
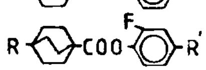
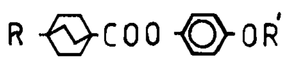
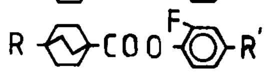
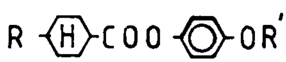
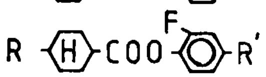
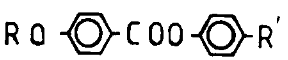
Ester	T_{NI} (°C)	$\Delta\varepsilon$	Δn	V_c (V)	M_{20}	M'_{20}	$-\frac{1}{V_c}\left(\frac{dV_c}{dT}\right)$ (%/°C)
	54	2.22	0.086	2.36	1.62	1.25	0.36
	87	1.69	0.102	3.24	1.69	1.29	0.13
	53	1.80	0.087	2.65	1.68	1.27	0.33

TABLE IV

Temperature dependencies and steepness of ester mixtures with $\Delta\epsilon \approx +2$

Ester	$-\frac{1}{V_c}\left(\frac{dV_c}{dT}\right)$ (% / °C)	M'_{20}
	0.36	1.25
	0.13	1.29
	0.33	1.27
	0.5	1.23
	0.4	1.24
	0.7	1.24
	0.6	1.28
	0.5	1.30

The most important feature of the data is the low temperature dependence associated with the BCO ring which is also characteristic of the cyano compounds.[3] For the alkyl/alkoxy ester mixture this is particularly low (0.13%/°C) compared with the values typical of other esters (a more exact comparison cannot be made because the same end groups could not be used).

The electro-optic steepness is comparable with other ester mixtures (M'_{20} 1.25 to 1.29) and was confirmed by measurements of the elastic constants. These were derived from the capacitance/voltage characteristics of homogeneously aligned cells.[6] The mixture of di-alkyl BCO esters and 2CB has $K_{33}/K_{11} = 1.1$ at 20°C, similar to the values for other esters. This is a second respect in which the esters (I) differ from the cyano compounds (II). In the latter the BCO ring significantly degrades threshold steepness and increases K_{33}/K_{11} to 3[3].

Twisted nematic electro-optic properties of low voltage multiplexing mixtures

The low temperature dependence and good steepness of the lightly doped mixtures of BCO esters makes them potentially useful for multiplexed displays. Low voltage multiplexing mixtures suitable for use in 7 μm twisted nematic devices operating from a 3 V supply (i.e. with $\Delta n \simeq 0.15$ and V_c at 20°C $\simeq$ 1, 1 V) were made by the addition of large percentages of cyanobiphenyls and PCH compounds.

The electro-optic properties in 7 μm twisted nematic devices of two ranges of mixtures, one containing between 22.5% and 45% di-alkyl BCO ester and the second containing between 25% and 40% alkyl/alkoxy BCO ester are shown in Figures 2 and 3. Their birefringences lie in the range 0.140 to 0.165 and threshold voltages at 20°C range from 1.0 V to 1.3 V.

The temperature dependencies are low (0.28 to 0.37%/°C) and this combined with good steepness ($M'_{20} < 1.35$) gives margins for 1:3 multiplexing between 9% and 11.5%. The 1:3 margins are defined as follows:

$$1{:}3 \text{ Margin} = \left\{\frac{1.92 - A}{1.92 + A}\right\}$$

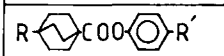
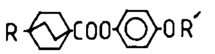
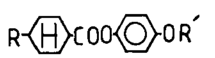
where

$$A = \frac{V_{50}(10°, 0°C)}{V_{90}(45°, 40°C)}$$

Lastly, in Table V the main properties of the BCO ester mixtures containing 30% di-alkyl and 30% alkyl-alkoxy ester are compared; data are also given for a typical mixture incorporating the more familiar and widely used alkyl/alkoxy cyclohexane esters. The mixtures using the new BCO esters are particularly suited for use in multiplexed displays and show a lower temperature dependence and a higher multiplexing margin than can be obtained using esters based on benzene and cyclohexane rings.

TABLE V

Electro-optic properties of mixtures containing 30% ester measured at 20°C

Ester	T_{NI} (°C)	Viscosity (cP) 20°C	0°C	Δn	V_c (V)	M'_{20}	$\frac{1}{V_c}\left(\frac{dV_c}{dT}\right)$ (%/°C)	1:3 Margin (%)
	80	39	147	0.160	1.12	1.34	0.33	9.9
	73	43	168	0.152	1.05	1.33	0.28	11.1
	60	35	124	0.147	1.01	1.36	0.40	9.0

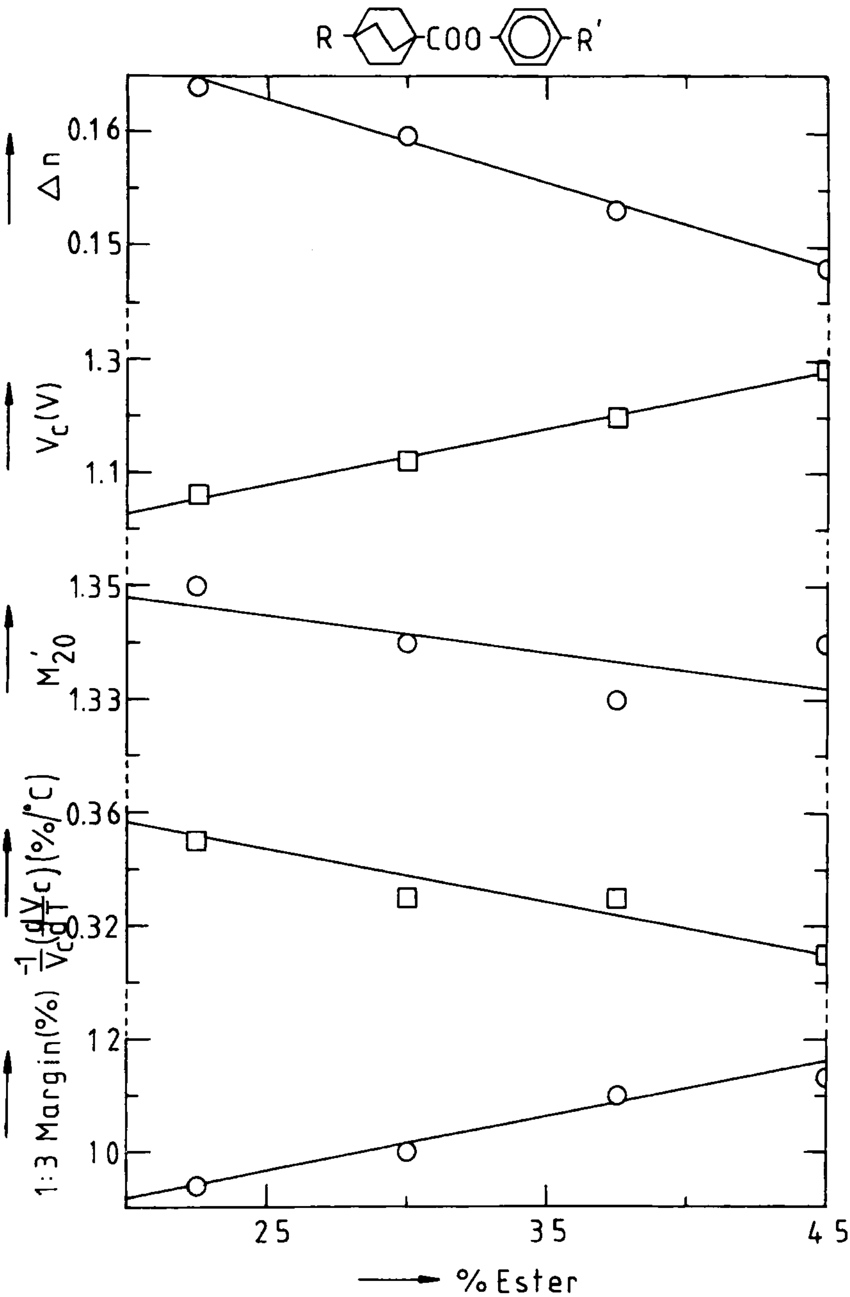


FIGURE 2 The main propeties of low voltage multiplexing mixtures containing dialkyl BCO esters.

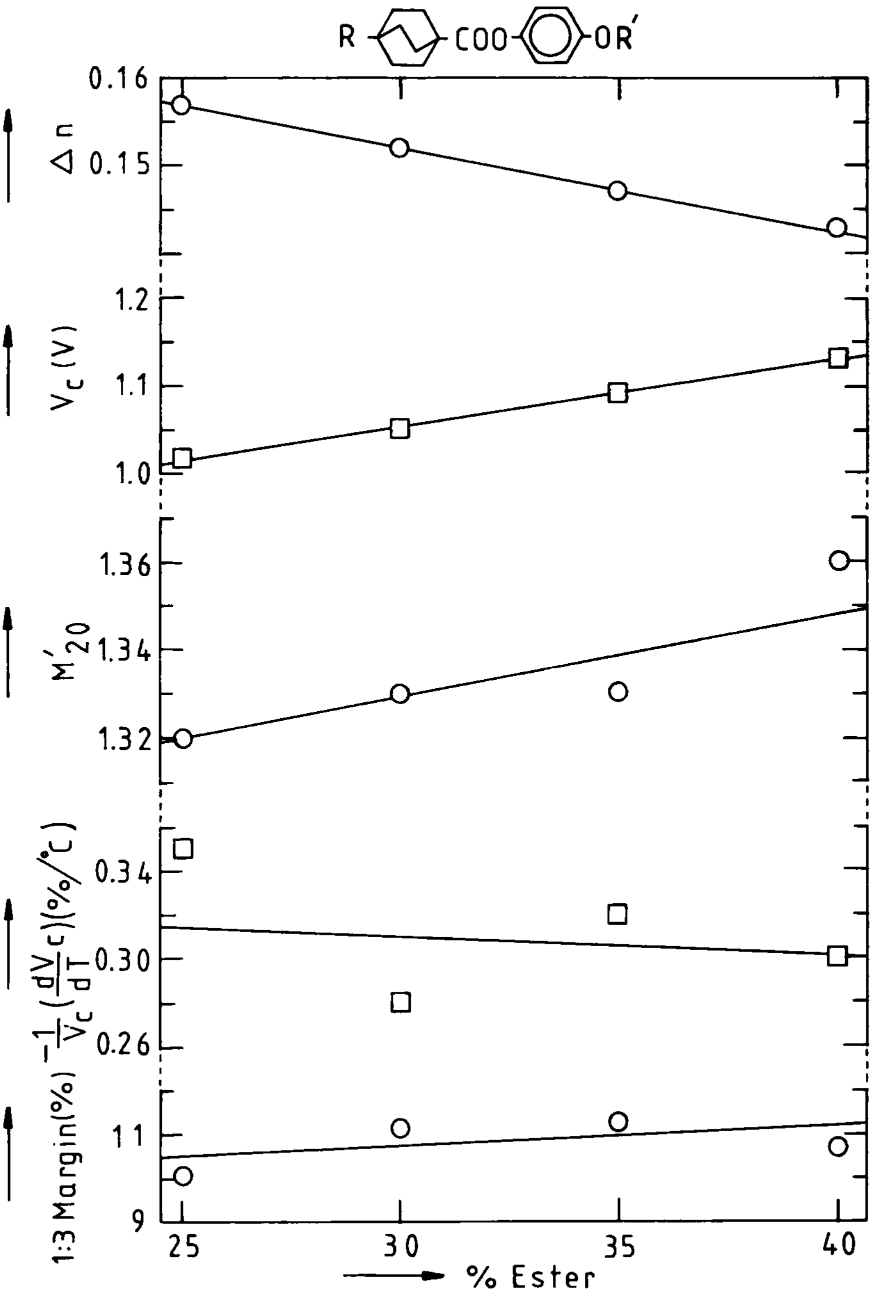


FIGURE 3 The main properties of low voltage multiplexing mixtures containing alkyl/alkoxy BCO esters.

Acknowledgements

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