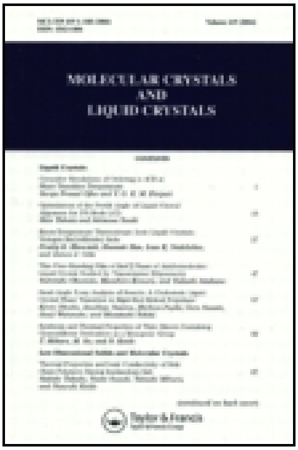

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Some New Mesogenic Esters Incorporating the 1,4-Disubstituted Bicyclo(2.2.2)octane Ring System

N. Carr [a] [b] , G. W. Gray [a] & S. M. Kelly [a] [c]

[a] Department of chemistry, The University, Hull, HU6 7RX, England

[b] Allen Clark Research Centre, Plessey Research (caswell) Limited, Caswell, Towcester, Northants, NN12 8EQ

[c] Brown Boveri Research Centre, CH-5405, Baden-Daettwil, Switzerland

Version of record first published: 20 Apr 2011.

To cite this article: N. Carr , G. W. Gray & S. M. Kelly (1985): Some New Mesogenic Esters Incorporating the 1,4-Disubstituted Bicyclo(2.2.2)octane Ring System, Molecular Crystals and Liquid Crystals, 130:3-4, 265-279

To link to this article: http://dx.doi.org/10.1080/00268948508079516

Mol. Cryst. Liq. Cryst., 1985, Vol. 130, pp. 265–279
0026-8941/85/1304–0265/$20.00/0

Some New Mesogenic Esters Incorporating the 1,4-Disubstituted Bicyclo(2.2.2)octane Ring System

N. CARR,† G. W. GRAY, and S. M. KELLY‡
Department of Chemistry, The University, Hull, HU6 7RX, England

(*Received February 24, 1985*)

A variety of one-ring, two-ring, and three-ring esters incorporating one or two 1,4-disubstituted bicyclo(2.2.2)octane rings has been synthesised. In some cases the esters are fully alicyclic, e.g., terminally alkyl substituted alkyl bicyclo-octanoates, bicyclo-octyl bicyclo-octanoates and bicyclo-octyl cyclohexanoates. In others, the acidic moiety consists of one or two benzene rings or a benzene ring linked to a cyclohexane ring. The range of esters also includes some alkyl and bicyclo-octyl esters in which the acidic moiety contains a bicyclo-octane linked to a benzene ring system. The transition temperatures for the different types of ester are reported and compared with one another and with literature values for related esters.

Results obtained from measurements of viscosity, birefringence, and electro-optical characteristics on some of the fully alicyclic esters are also reported.

INTRODUCTION

A large number of substituted phenyl esters of the alicyclic 4-n-alkylbicyclo(2.2.2)octane-1-carboxylic acids have been reported in the last few years.[1–6] Combinations of the physical properties of several classes of these bicyclo-octane esters[1–3] make them commercially interesting as components of nematic mixtures for certain electro-optic display applications[7–9] (especially the twisted nematic display with multiplexed addressing[7]).

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†Present address: Allen Clark Research Centre, Plessey Research (Caswell) Limited, Caswell, Towcester, Northants, NN12 8EQ

‡Present address: Brown Boveri Research Centre, CH-5405, Baden-Daettwil, Switzerland

A wide variety of esters of the more common alicyclic ring system—*trans*-1,4-disubstituted cyclohexane—have also been synthesised.[10-16] Many of these esters exhibit wide-range nematic phases,[10-13] and are used as components in nematic mixtures for the twisted nematic display.[10,11,13] Completely alicyclic esters consisting of two *trans*-1,4-disubstituted cyclohexane rings[13] are also of commercial interest for the "guest-host" device[17] and a special form of the twisted nematic display[18] where low birefringence is required.

Work was undertaken to extend our study of mesogens incorporating the 1,4-disubstituted bicyclo(2.2.2)octane ring system to include a number of fully alicyclic esters analogous to those described above. The required 1-alkyl-4-hydroxybicyclo(2.2.2)octanes were also interacted with a variety of other acids to yield a range of esters. The values obtained for the liquid crystal transition temperatures of these novel esters derived from a bicyclo-octanol extend the limited results reported in the literature[19] for such esters.

RESULTS AND DISCUSSION

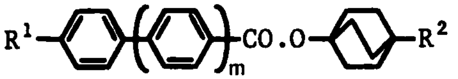
The transition temperatures for six esters [(I) and (II)] derived from 4-alkylbicyclo(2.2.2)octan-1-ols and 4-alkyl-/alkoxy-benzoic acids (m = 0) or 4'-alkylbiphenyl-4-carboxylic acids (m = 1) are listed in Table I. As usual, the alkoxy-substituted esters exhibit higher clearing points (T_{N-I}) than the alkyl substituted esters [(I); m = 0]. Whereas, the T_{N-I} values of the esters (I) are only marginally lower (*ca.* −1.5°C) than those of the corresponding esters with the ester group reversed,[3] the melting points are significantly higher (*ca.* +44.5°C, on average). Thus, the nematic ranges of the esters (I) are much shorter than those of their structural isomers.[3] As is usually the case, the clearing points of the esters [(II); m = 1] containing an additional benzene ring are much higher (*ca.* +125°C) than those of the esters (I); the melting points are higher by *ca.* +50°C. A smectic A—nematic transition is exhibited at an elevated temperature by one of the esters (II).

Esters of 6-pentyl-2-naphthoic acid and 1-hydroxy-4-propyl-, and 1-hydroxy-4-pentyl-bicyclo(2.2.2)octane have the following liquid crystal transitions (C-N, 98°C; N-I, 131°C; and C-N, 90.5°C; N-I, 128.5°C, respectively) intermediate in temperature between those of the corresponding benzoates and biphenyl-4-carboxylates [(I) and (II)]. This is consistent with results obtained for related series of esters.[2]

The liquid crystal transition temperatures for the fully alicyclic esters (III) derived from 4-alkylbicyclo(2.2.2)octan-1-ols and *trans*-

TABLE I

Transition temperatures (°C) for compounds of structure



(I) and (II)

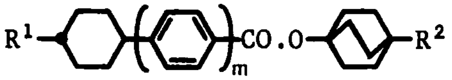
n-R^1	n-R^2	m	C-S_A/N/I	S_A-N	N-I
C_5H_{11}	C_3H_7	0	99.5	-	[49]
C_5H_{11}	C_5H_{11}	0	68	-	(59)
C_4H_9O	C_3H_7	0	87	-	98
C_4H_9O	C_5H_{11}	0	83	-	98
C_5H_{11}	C_3H_7	1	144	-	200
C_5H_{11}	C_5H_{11}	1	128.5	131	202

( ) denotes a monotropic transition
[ ] denotes a virtual transition

4-alkylcyclohexane-1-carboxylic acids are recorded in Table II. The esters (III) exhibit unusually low melting points, at or below room temperature, and high T_{S_B}-I values. These are reminiscent of the high T_{S_B}-I values for the 1,2-(di-*trans*-4-alkylcyclohexyl)ethanes, and in both cases, the stable S_B phases presumably arise from purely Van der Waals interactions. Only one ester [(III), 5/3] exhibits an enantiotropic nematic phase, and virtual nematic-isotropic transition temperatures had to be determined for the other esters. These were obtained in the usual way[20] and lie just below the T_{S_B}-I values. The same procedure was applied to the 5/3 ester, and the correspondence between the value obtained and the real T_{N-I} value lends support to the procedure involved. Typical of the whole series, this ester exhibits smectic and nematic phases which persist until significantly higher temperatures (S_B-I, 79°C and N-I, 92°C) than those of the corresponding esters with either a cyclohexane ring (S-N, 37°C and N-I, 52°C)[13] or a benzene ring (N-I, 43°C)[10] in place of the bicyclo-octane ring. The transition temperatures are also higher than those of the corresponding esters (I) with a benzene ring in place of the cyclohexane ring (see Table I).

TABLE II

Transition temperatures (°C) for compounds of structure



(III) m = 0 and
(IV) m = 1

n-R^1	n-R^2	m	C-S_B/N	S_B-N/I	N-I
CH_3	C_5H_{11}	0	22	49	[40]
C_2H_5	C_5H_{11}	0	4	73	[59]
C_3H_7	C_5H_{11}	0	1	88	[85]
C_4H_9	C_5H_{11}	0	9	104.5	[92]
C_5H_{11}	C_5H_{11}	0	-3	107	[100]
C_6H_{13}	C_5H_{11}	0	19	115	[102]
C_7H_{15}	C_5H_{11}	0	11	114	[103]
C_5H_{11}	C_3H_7	0	18	79	92
C_5H_{11}	C_3H_7	1	144	-	186
C_5H_{11}	C_5H_{11}	1	114	131	201

[ ] denotes a virtual transition

The liquid crystal transition temperatures for the homologous series of 4-pentylbicyclo(2.2.2)octyl *trans*-4-alkylcyclohexane-1-carboxylates are plotted against the number of carbon atoms in the terminal alkyl chain in Figure 1. The virtual T_{N-I} values and the T_{S_B}-I values increase with increasing chain length. The normal pattern of alternation in the opposite sense is observed for the T_{S_B}-I and the T_{N-I} values (see Figure 1).[21] The regular alternation and the smooth curves for the virtual T_{N-I} values in Figure 1 lend further support to the meaningfulness of these values. These virtual T_{N-I} values were determined by extrapolation of values obtained for mixtures of each individual ester (III) and the commercially available nematic mixture E7.[20] The esters are very soluble in the mixture, and binary mixtures consisting of up to 90 wt % of the esters could be prepared and were

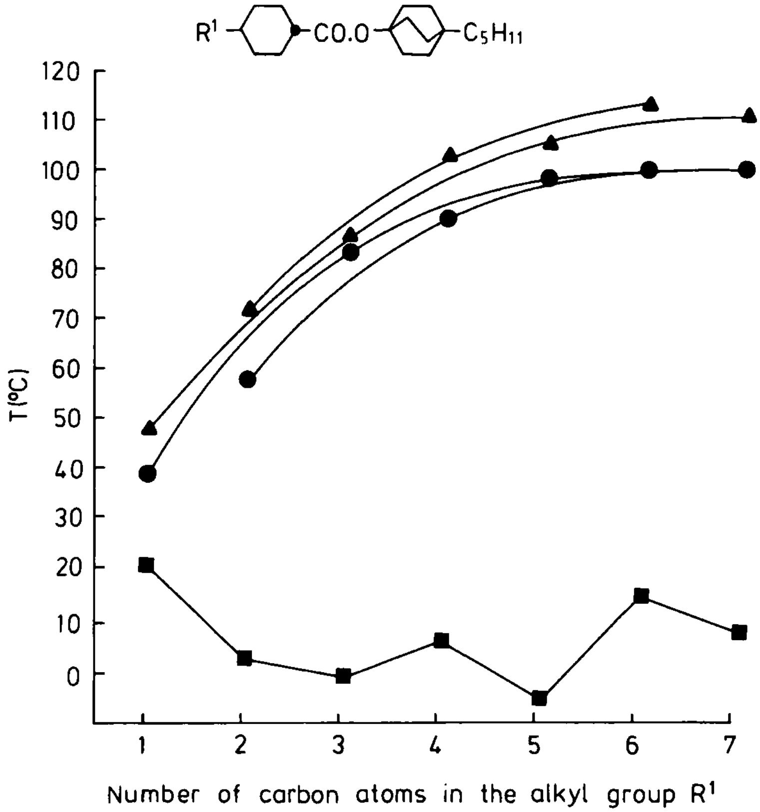


FIGURE 1 Plot of transition temperature against the number of carbon atoms in the alkyl chain R of the esters formulated: ●, virtual nematic-isotropic liquid; ▲, smectic B-isotropic liquid; ■, crystal-smectic B.

still found to exhibit a nematic phase. Plots of the clearing points (T_{N-I}) for such mixtures against percentage composition are shown in Figure 2 for a homologous series of the esters (III). These plots are all similar in shape and are strongly non-linear. These plots are consistent with previous results[22,23] which have shown that not all of the physical properties (including the clearing point) for mixtures of liquid crystal materials obey the simple additivity rule and that substantial deviations from ideal linear behaviour are to be observed. If the extrapolation procedure were applied to those portions of the curves in Figure 2 corresponding to a *low* percentage of E7 in the mixture, the extrapolated T_{N-I} for E7 would be much below 60°C—around 20–35°C. In these dilute solutions of E7 in the ester, the

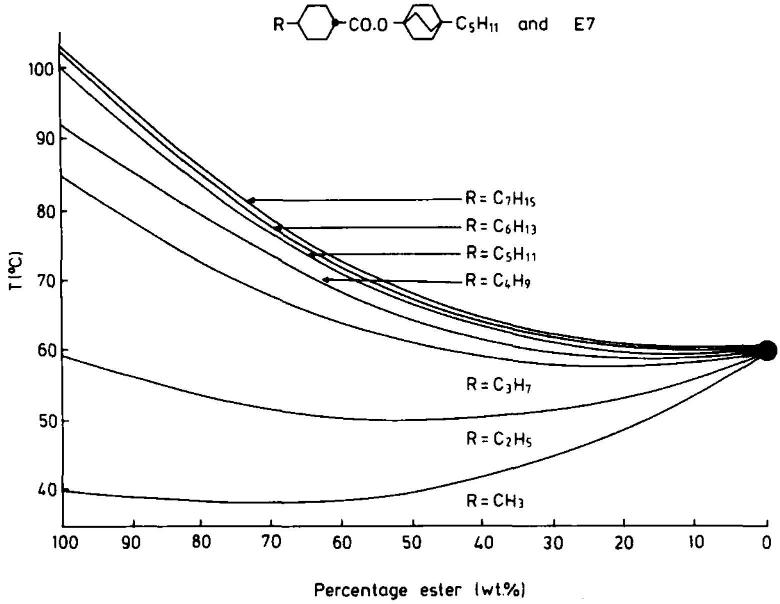


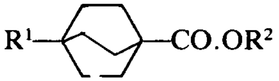
FIGURE 2 Plot of T_{N-I} against composition (wt %) for mixtures of individual homologues of the structure formulated with the nematic mixture E7. Extrapolation was minimised by including measurements on as concentrated solutions (frequently 90 wt %) of ester in E7 as possible.

cyano-substituted components of E7 are presumably largely not anti-parallel correlated, and the higher *actual* T_{N-I} for E7 must reflect the effect of anti-parallel correlation in enhancing T_{N-I} in pure E7 and in mixtures of E7 containing a low concentration of ester.

The transition temperatures for two related benzoate esters (IV) containing an additional benzene ring are also shown in Table II. They are very similar to those of the analogous esters (II)—Table I—with a benzene ring in place of the cyclohexane ring, and the same comments are valid. It is noted however that the smectic phase has changed from S_A in series (II) to S_B in series (IV).

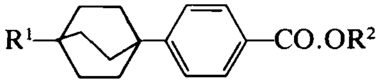
Comparing homologues with equal lengths of the terminal chains, the change from structure [(III); m = 0] to [(IV); m = 1] has increased T_{N-I} much more (*ca.* +100°C) than $T_{S_B\text{-}N/I}$ (*ca.* +25°C), but the melting points have been increased by *ca.* +120°C.

The transition temperatures for a further range of esters incorporating the 1,4-disubstituted bicyclo(2.2.2)octane ring are recorded in Table III. Simple alkyl esters of 4-alkylbicyclo(2.2.2)octane-1-carboxylic acid [(V); m = p = o]



[(V); m = p = o—see Table III]

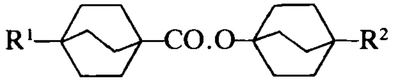
exhibit very low virtual clearing points (*ca.* – 100°C). The presence of an additional 1,4-disubstituted benzene ring in the acid part of the esters [(VI); m = 1; p = 0]



[(VI); m = 1; p = 0—see Table III]

produces esters with very much higher clearing points (30° – 85°C). From the data for the few homologues prepared, it appears that the clearing point decreases as the length of the alkyl chain increases in a homologous series of the esters (VI).

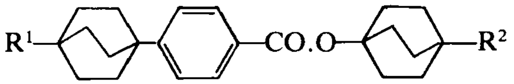
The fully alicyclic esters (VII) containing two bicyclo-octane rings (m = 0; p = 1)



[(VII); m = 0; p = 1—see Table III]

possess very wide range smectic phases (S_B); melting occurs at, or just above, room temperature, and the clearing points (S_B-I, *ca.* 185° – 195°C) are very high. Extrapolated T_{N-I} values (virtual) for these compounds are the highest recorded for such simple esters (*ca.* 120° – 130°C). The analogous compounds without an ester linkage[24] exhibit much lower melting points (e.g., 5/5; C-S, 47°C) and somewhat higher clearing points (e.g., 5/5; S-I, 247°C) as judged by the few homologues reported.

The presence of an additional benzene ring in the acid part gives the esters [(VIII); m = p = 1]



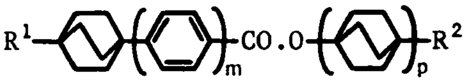
[(VIII); m = p = 1—see Table III]

which have very high melting points (*ca.* 175° – 195°C) and clearing points (*ca.* 220° – 235°C), although no smectic phases were observed.

The transition temperatures for a number of esters with identical alkyl chains (with one exception), which otherwise differ only in the presence of a 1,4-disubstituted benzene, *trans*-cyclohexane, and bicyclo(2.2.2)octane ring are collated in Table IV. The totally aromatic phenyl benzoate ester exhibits the lowest T_{N-I}, whilst the totally alicyclic ester containing two bicyclo-octane rings exhibits the highest T_{N-I} (virtual). Esters containing aromatic and alicyclic rings possess intermediate T_{N-I} values, those containing a bicyclo-octane ring exhibiting higher clearing points than the corresponding cyclohexane esters.

TABLE III

Transition temperatures (°C) for some compounds of structure

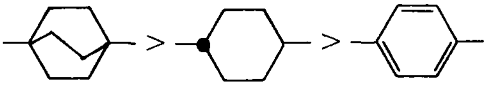


(V) - (VIII)

n-R^1	n-R^2	m	p	C-S_B/N/I	S_B-I	N-I
C_3H_7	C_3H_7	0	0	-	-	[-97]
C_5H_{11}	C_3H_7	0	0	-	-	[-105]
C_5H_{11}	C_5H_{11}	0	0	-	-	[-110]
C_3H_7	CH_3	1	0	110.5	-	[83]
C_3H_7	C_3H_7	1	0	81.5	-	[39]
C_5H_{11}	C_3H_7	1	0	87	-	[49]
C_5H_{11}	C_5H_{11}	1	0	85	-	[32]
C_4H_9	C_5H_{11}	0	1	38	186	[119]
C_5H_{11}	C_5H_{11}	0	1	40	191.5	[130]
C_6H_{13}	C_5H_{11}	0	1	20	192.5	[118]
C_5H_{11}	C_3H_7	1	1	192	-	235
C_5H_{11}	C_5H_{11}	1	1	176	-	218

[ ] denotes a virtual transition

The values for T_{N-I} listed in the Tables I–IV and those available from the literature for the corresponding esters containing benzene[25] or cyclohexane rings[10,15] yield the usual order[2] of decreasing clearing point:



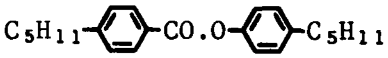
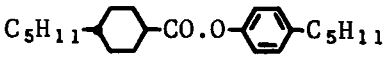
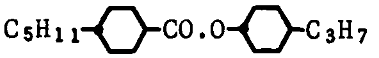
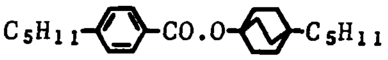
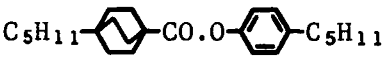
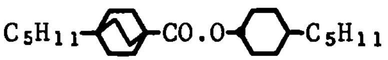
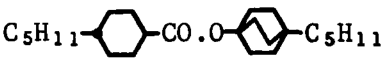
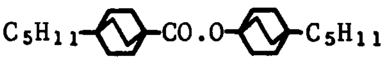
PHYSICAL PROPERTIES

Viscosity

The viscosity of one homologue of structure [(V); m = p = 0]—the propyl ester of 4-propylbicyclo(2.2.2)octane-1-carboxylic acid—was

TABLE IV

Comparative transition temperatures (°C) for some related esters

Structure	C-S_B/N/I	S_B-N	N-I	Ref.
	36	-	(26)	25
	37	-	48	15
	25	37	52	10
	68	-	(59)	*
	31	-	64.5	3
	17	96	[92]	26
	-3	107	[100]	*
	40	191.5	[130]	*

( ) denotes a monotropic transition
[ ] denotes a virtual transition
*current work

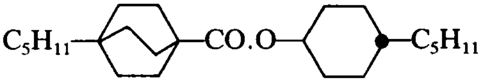
determined and found to be low ($\eta_{20^\circ C}$, 9 cSt; $\eta_{0^\circ C}$, 18 cSt; both values relate to the isotropic phase). The viscosity of one homologue (5/5) of the bicyclo-octyl benzoate esters [(I); m = 0] was found to be large ($\eta_{20^\circ C}$, 100 cSt; extrapolated value for the nematic phase). This value is much higher than that ($\eta_{20^\circ C}$, *ca.* 35 cSt extrapolated value for the nematic phase) for the corresponding ester with the ester linkage reversed.

Birefringence

The birefringence of one alicyclic member (5/3) of the bicyclo-octyl cyclohexanoates [(III); m = 0] was, as expected, very low (Δn, 0.036 at 0.98 × T_{N-I} for the nematic melt.

Electro-optic properties

The bicyclo-octyl cyclohexanoates have quite a high solubility in various nematic hosts, and the electro-optic characteristics of one such solution have been assessed (see Table V). For comparison, in this Table and also in Table VI are quoted some related results for a cyclohexyl bicyclo-octanoate[26] (IX)



(IX)

and also for some esters that are used commercially as additives in mixtures for multiplexing.

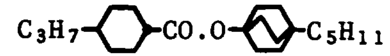
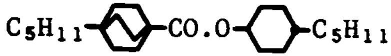
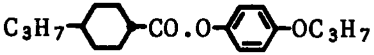
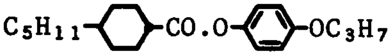
Compared with esters used commercially as additives, e.g., dialkyl or alkyl/alkoxy substituted phenyl cyclohexanoates, the purely alicyclic esters stand up fairly well. The effects on T_{N-I}, viscosity, M_{20}, M'_{20}, and $V_{90}(45^\circ)$ are moderate, whilst birefringence values are lowered considerably. For example, the birefringence of ZLI 1132 is reduced by 0.022 by the addition of 20 wt % of ester (IX).

However, the most marked effect of these esters as additives is the lowering of the temperature dependence of the threshold voltage of the host. Relative to the phenyl cyclohexanoates, the purely alicyclic esters have a greater effect in reducing $-1/V(dV/dT)$ for the hosts E7 and ZLI 1132; the effects are comparable for host ZLI 1289—see Tables V and VI.

Reductions in $-1/V(dV/dT)$ values for nematic hosts are also known to occur when substituted phenyl bicyclo-octanoates and phenylbicyclo-octanes are used as low Δε additives, and in view of the results for the purely alicyclic esters now being discussed, it is natural to relate the effects to the presence in the molecules of the additive of

TABLE V

Electro-optic properties of solutions of esters in ZLI 1289†

Mixture	T_{N-I} (°C)	$-\frac{1}{V}\left(\frac{dV}{dT}\right)$ (% °C^{-1})	$V_{90}(45°)$ (V)	M_{20}	M'_{20}
ZLI 1289	64	0.47	0.91	1.87	1.33
ZLI 1289 + 30 wt % of 	59	0.40	1.05	1.77	1.34
ZLI 1289 + 30 wt % 	64	0.40	1.05	1.77	1.33
ZLI 1289 + 15 wt % of each of  	60	0.40	1.01	1.79	1.36

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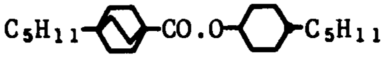
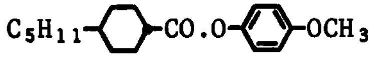
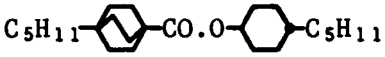
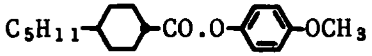
†A commercial nematic mixture of E. Merck, Darmstadt, F.R.G

TABLE VI

Viscosities and temperature dependences of threshold voltage for some nematic mixtures

Mixture	T_{N-I} (°C)	$-\frac{1}{V}\left(\frac{dV}{dT}\right)$ (% °C^{-1})	$\eta_{20°C}$ (cP)
E7†	57.3	0.75	37.8
E7 + 20 wt % of 	57.2	0.65	37.6
E7 + 20 wt % of 	58.6	0.72	33.2
ZLI 1132*	71.5	0.55	28.1
ZLI 1132 + 20 wt % of 	70.2	0.44	28.2
ZLI 1132 + 20 wt % of 	68.9	0.52	24.2

† A commercial nematic mixture of B.D.H. Chemicals Ltd., Poole, U.K.
* A commercial nematic mixture of E. Merck, Darmstadt, F.R.G

the 1,4-disubstituted bicyclo(2.2.2)octane ring system.

The dialkyl substituted bicyclo-octyl cyclohexanoates and cyclohexyl bicyclo-octanoates are therefore of interest for use in multiplexible mixtures, particularly if low values of birefringence and temperature dependence of threshold voltage are important. Their main disadvantage is their strong smectic characteristics; however, since the phases given by the pure esters are S_B, this is not a problem in mixtures in hosts whose components are terminally cyano-substituted and tend to be S_A in their tendencies. In the mixtures, the S_B properties are therefore strongly repressed, and the nematic properties are dominant.

EXPERIMENTAL

Structure and purity of materials

Infra-red, ^1H n.m.r., and mass spectra were obtained for the compounds prepared and were found, in each case, to be consistent with the required structure. The instruments employed were, respectively, a Jeol JNM-4H × 100 spectrometer, a Perkin Elmer 457 spectrophotometer, and an AEI MS 902 mass spectrometer. Each ester gave a single-spot on thin layer chromatography (t.l.c.). Analysis of the esters by gas-liquid chromatography (g.l.c.) indicated purities of at least 99.7% and values of 99.9% were usual.

Preparation of materials

The esters [(I)–(VIII)] were prepared by esterification of the acid chlorides of the appropriate acids (prepared according to literature methods[3,5,12]) with the required alcohols,[15,20] according to literature methods.[3] The purification procedures have already been described.[3]

Transition temperatures

The liquid crystal transition temperatures of the esters recorded in Tables I–IV were determined by optical microscopy using either a Vickers M72c polarising microscope or a Nikon L-Ke polarising microscope in conjunction with a Mettler FP52 heating stage and an FP5 control unit. The Mettler stage could be cooled (to $< -20°C$) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage. Several transition temperatures, particularly crystal to smectic B (C-S_B) transition temperatures, were determined using a Perkin-Elmer DSC-2C differential scanning calorimeter. For those cases where it was not possible to observe a liquid crystal transition directly, virtual nematic-isotropic (N-I) transition temperatures were determined in the normal manner.[20]

Smectic A and B phases were characterised by their optical textures and normal miscibility methods.

CONCLUSION

Some thirty esters of various types incorporating the 1,4-disubstituted bicyclo(2.2.2)octane ring system have been synthesised. Comparison of the transition temperatures for these esters and similar esters containing 1,4-disubstituted benzene and *trans*-cyclohexane rings show that (i) the T_{N-I} values (in some cases virtual) are highest for fully alicyclic esters, (ii) esters containing bicyclo-octane rings instead of cyclohexane rings exhibit the higher clearing points (N-I), and (iii) the T_{S_B}-N values for esters containing two alicyclic rings are also very high, and in many cases nematic phases cannot be observed for such esters, i.e., the transitions are S_B-I.

The plots of T_{N-I} for mixtures of several of these esters with E7 are strongly non-linear. This emphasises the necessity of minimising the extent of extrapolation when determining virtual values for transition temperatures.

Acknowledgments

This paper is published by permission of the Director HMSO and the authors thank the U.K. Ministry of Defence for a research grant. Colleagues at R.S.R.E. (Malvern) and E. Merck (Darmstadt) are thanked for permission to publish electro-optic data. The authors are also grateful to B.D.H. Chemicals Limited (Poole) for the supply of larger amounts of 4-hydroxy-1-propyl- and -1-pentylbicyclo(2.2.2)octane than we could conveniently synthesise.

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