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The Liquid Crystal Properties of 4-n-Alkyl- and 4-n-Alkoxy-phenyl 4-n-Alkylbicyclo (2.2.2) octane-1-carboxylates

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The Liquid Crystal Properties of 4-*n*-Alkyl- and 4-*n*-Alkoxy-phenyl 4-*n*-Alkylbicyclo(2.2.2)octane-1-carboxylates

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(*Received February 16, 1981*)

Two new series of esters incorporating the 1,4-disubstituted bicyclo(2.2.2)octane ring system are reported. Thirty-three 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates and thirty 4-*n*-alkoxyphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates have been prepared and found to exhibit wide-range nematic phases persisting until higher temperatures than those of the corresponding esters containing either the *trans*-1,4-disubstituted cyclohexane ring or the 1,4-disubstituted benzene ring in place of the bicyclo-octane ring. Mixtures of these novel bicyclo-octane esters with cyanobiphenyls have been found to be superior for multiplexing applications in twisted nematic cells to equivalent mixtures employing 4-*n*-alkylphenyl 4-*n*-alkoxybenzoates or 4-*n*-alkoxyphenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates.

INTRODUCTION

During the last two years, much of the work in our laboratories has been concerned with further liquid crystalline materials containing the 1,4-disubstituted bicyclo(2.2.2)octane ring system. This interest has developed from our earlier studies[1-3] of bicyclo(2.2.2)octane systems with terminal nitrile functions, i.e., materials which were of high positive dielectric anisotropy in the nematic phase. Mesogenic derivatives of bicyclo-octane (some also with terminal nitrile groups) were also the subject of papers presented by us at the Kyoto Conference, and this information will be published in the near future.[4]

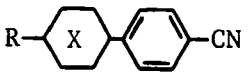
Although the gradients of the transition lines obtained on plotting the nematic-isotropic transition temperatures (T_{N-I}) against the alkyl chain length differ substantially from series to series of the bicyclo-octane materials that have been studied, and this makes comparisons difficult for very early homologues (see later), the most significant aspect of the studies of the terminally

cyano-substituted bicyclo-octanes is that in the great majority of cases the T_{N-I} values for the bicyclo-octane compounds are very significantly *higher* than those of the corresponding compounds in which the bicyclo-octane ring is replaced by a *trans*-1,4-disubstituted cyclohexane ring or a 1,4-disubstituted benzene ring.

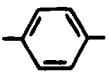
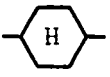
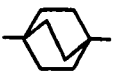
The following examples in Tables I and II illustrate the magnitude of the

TABLE I

Comparative data[1,3,5,6] for systems of the general structure



(I)

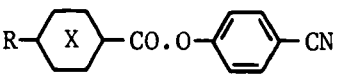
X   

R	C—N or I (°)	N—I (°)	C—N (°)	N—I (°)	C—N (°)	N—I (°)
C_3H_7	68	(25.5)	36	46	66.5	88
C_5H_{11}	22.5	35	31	55	62	100
C_7H_{15}	28.5	42	30	59	61	95

( ) Monotropic transition.

TABLE II

Comparative data[2,4,7,8] for systems of the general structure



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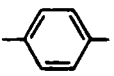
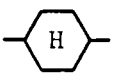
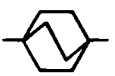
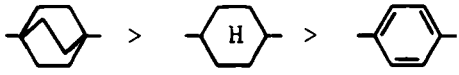
X   

R	C—N or I (°)	N—I (°)	C—N (°)	N—I (°)	C—N or I (°)	N—I (°)
C_4H_9	67	(42.5)	56	68	99	(96)
C_5H_{11}	64.5	[58]	47	79	89	109
C_6H_{13}	44.5	47	49.5	71	77	102
C_7H_{15}	44	57	54	83.5	54	106

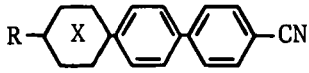
( ) Monotropic transition.
[ ] Virtual transition temperature.

effects that have been observed for compounds of the general structure ((I) and (II)).

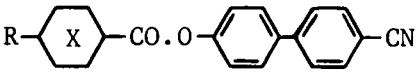
These, and other examples,[4] define the order of decreasing T_{N-I} as follows:



As already reported,[9] however, when the T_{N-I} values are high, as in the case for compounds with the general structures (III) and (IV) below,



(III)



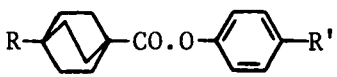
(IV)

where ring X may be bicyclo-octane, cyclohexane, or benzene, the relative positions of cyclohexane and benzene in the above order are either reversed (III) or about equal (IV).

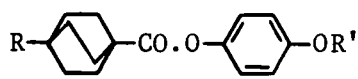
In other papers presented at the Kyoto Conference, the implications of these observations are discussed,[4] but for the present purposes, the important fact is that the T_{N-I} values of the bicyclo(2.2.2)octane compounds are consistently higher than those of the corresponding cyclohexane and benzene systems, except possibly, as already mentioned, when methyl and ethyl homologues are involved.

The other significant factor to emerge from the study of the cyano-substituted bicyclo-octanes was the low temperature dependence of the threshold voltage of nematic mixtures of the 1-n-alkyl-4-(4′-cyanophenyl)bicyclo(2.2.2) octanes in twisted nematic cells. These results and other features of the electro-optical properties of these bicyclo-octanes were reported[10] at the Kyoto Conference by our colleagues from the Royal Signals and Radar Establishment.

These general results encouraged us to examine the bicyclo-octane esters ((V) and (VI)) with terminal *n*-alkyl and *n*-alkoxy groups.

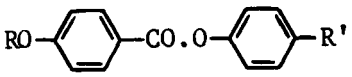


(V)

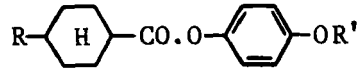


(VI)

The decision to prepare the bicyclo-octane esters ((V) and (VI)) was strongly influenced by the fact that the analogous 4-*n*-alkylphenyl 4-*n*-alkoxybenzoates[11] (VII) and the 4-*n*-alkoxyphenyl *trans*-4-*n*-alkylcyclohexane-1-carboxylates[8] (VIII) are



(VII)



(VIII)

of considerable commercial interest because their admixture with materials of high positive dielectric anisotropy gives nematic phases which function well in twisted nematic displays with a multiplexed drive.[12,13] The aim of this work was, therefore, to produce nematogenic bicyclo-octane esters ((V) and (VI)) with similar electro-optical properties to the analogous benzoate and cyclohexanoate esters ((VII) and (VIII)), but with significantly higher T_{N-I} values and *perhaps* a much lower dependence of threshold voltage on temperature. If the novel bicyclo-octane esters ((V) and (VI)) did exhibit such physical properties, then they might be of considerable commercial interest for multiplexed electro-optical display devices.

RESULTS AND DISCUSSION

Preliminary results for a few homologues of these two series of bicyclo-octane esters have been reported briefly elsewhere.[14] However, complete data for thirty-three dialkyl bicyclo-octane esters (V) and thirty alkyl/alkoxy esters (VI) are now recorded in Tables III and IV respectively. Typical examples of how the transition temperatures change with lengthening alkyl chain are shown in Figures 1 and 2. The dialkyl bicyclo-octane esters (V) are exemplified in Figure 1 (for R, *n*-C_5H_{11}). All the curves for this series possess this concave shape and presumably with longer chains would reach a maximum before falling again. The alkyl/alkoxy bicyclo-octane esters (VI) are exemplified in Figure 2 (for R, *n*-C_7H_{15}). In this case the T_{N-I} curve is slightly convex; in other cases the degree of convexity is more pronounced, whereas other series may exhibit concave curves similar to those shown in Figure 1.

The results recorded in Tables III and IV illustrate the types of smectic phase which have been observed and the lateness in the series of both types of ester at which these smectic properties occur, i.e., the majority of the esters examined are purely nematic (twenty-five out of thirty-three dialkyl esters (V) and twenty-five out of thirty alkyl/alkoxy esters (VI)). When smectic phases are observed (for long alkyl chain lengths), these are S_B phases in the case of

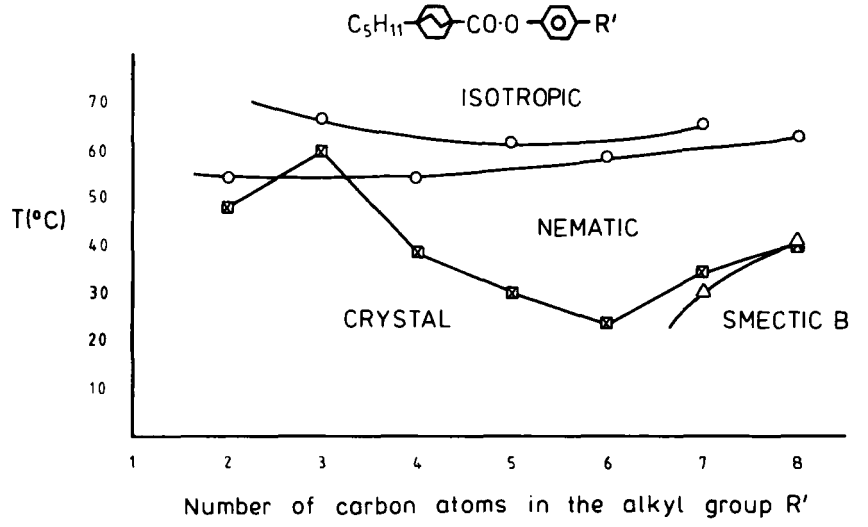


FIGURE 1 Plot of the transition temperatures against number of carbons in the alkyl chain R' of the esters formulated: O, nematic-isotropic liquid transition; Δ, smectic B-nematic transition; ⊠, crystal-smectic B or nematic transition.

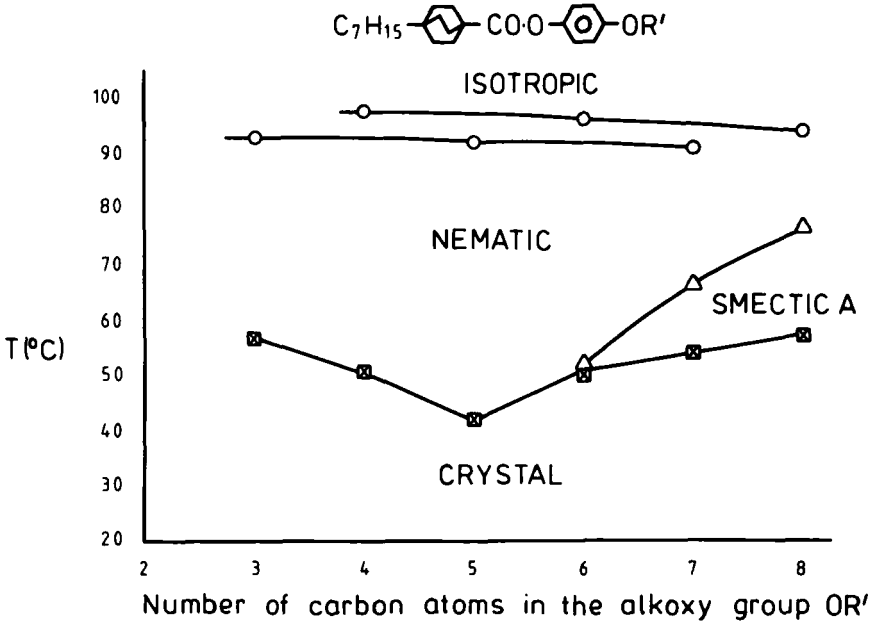
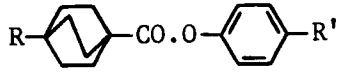


FIGURE 2 Plot of the transition temperatures against number of carbons in the alkyl chain R' of the esters formulated: O, nematic-isotropic liquid transition; Δ, smectic A-nematic transition; ⊠, crystal-smectic A or nematic transition.

TABLE III

Data for the compounds of structure



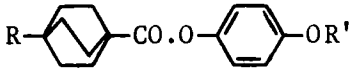
(V)

		Transition temperatures (°C)		
n-R	*n*-R′	C—S_B/N/I	S_B—N	N—I
C_3H_7	C_3H_7	67	—	[61]
C_3H_7	C_4H_9	57	—	(44)
C_3H_7	C_5H_{11}	29.5[a]	—	55.5
C_3H_7	C_6H_{13}	47.5	—	(45.5)
C_3H_7	C_7H_{15}	52.5	—	53
C_3H_7	C_8H_{17}	8	—	53
C_4H_9	C_2H_5	49	—	(35.5)
C_4H_9	C_3H_7	50	—	(47)
C_4H_9	C_4H_9	38.5	—	(38)
C_4H_9	C_5H_{11}	30	—	49
C_4H_9	C_6H_{13}	28.5	—	43
C_4H_9	C_7H_{15}	23	—	52
C_4H_9	C_8H_{17}	26.5	—	50.5
C_5H_{11}	C_2H_5	48	—	55
C_5H_{11}	C_3H_7	59.5	—	66.5
C_5H_{11}	C_4H_9	38.5	—	54
C_5H_{11}	C_5H_{11}	31[b]	—	64.5
C_5H_{11}	C_6H_{13}	23.5	—	58.5
C_5H_{11}	C_7H_{15}	34.5	(30.5)	65
C_5H_{11}	C_8H_{17}	41	41.5	62.5
C_6H_{13}	C_2H_5	44.5	—	47.5
C_6H_{13}	C_3H_7	41	—	60
C_6H_{13}	C_4H_9	46.5	—	51
C_6H_{13}	C_5H_{11}	38	—	54.5
C_6H_{13}	C_6H_{13}	40	(33)	54
C_6H_{13}	C_7H_{15}	44[c]	(36)	57
C_6H_{13}	C_8H_{17}	48	(52.5)	59.5
C_7H_{15}	C_3H_7	58.5	—	71
C_7H_{15}	C_4H_9	34	—	53
C_7H_{15}	C_5H_{11}	33	—	62
C_7H_{15}	C_6H_{13}	27	42.5	60
C_7H_{15}	C_7H_{15}	34.5	53.5	69
C_7H_{15}	C_8H_{17}	34	61	67

( ) Monotropic transition
[ ] Virtual transition temperature
[a] ΔH, 30.7 kJ mol^{-1}
[b] ΔH, 29.8 kJ mol^{-1}
[c] ΔH, 34.1 kJ mol^{-1}

TABLE IV

Data for compounds of the structure



(VI)

n-R	*n*-R'	Transition temperatures (°C) C—S_A/N/I	S_C—S_A	S_A—N	N—I
C_3H_7	C_3H_7	61	—	—	89
C_3H_7	C_4H_9	48[a]	—	—	94
C_3H_7	C_5H_{11}	40	—	—	87
C_3H_7	C_6H_{13}	73.5	—	—	90.5
C_3H_7	C_7H_{15}	50	—	—	85
C_3H_7	C_8H_{17}	52	—	—	87.5
C_4H_9	C_3H_7	49	—	—	81.5
C_4H_9	C_4H_9	32.5	—	—	84.5
C_4H_9	C_5H_{11}	51.5	—	—	85
C_4H_9	C_6H_{13}	46	—	—	88
C_4H_9	C_7H_{15}	53	—	—	84
C_4H_9	C_8H_{17}	44.5	—	—	83
C_5H_{11}	C_3H_7	41	—	—	95
C_5H_{11}	C_4H_9	42[b]	—	—	100
C_5H_{11}	C_5H_{11}	50.5	—	—	93.5
C_5H_{11}	C_6H_{13}	54.5	—	—	97
C_5H_{11}	C_7H_{15}	57	—	—	93
C_5H_{11}	C_8H_{17}	53.5	(37)	(49.5)	95.5
C_6H_{13}	C_3H_7	62.5	—	—	87.5
C_6H_{13}	C_4H_9	48	—	—	93.5
C_6H_{13}	C_5H_{11}	47	—	—	84
C_6H_{13}	C_6H_{13}	47.5	—	—	86
C_6H_{13}	C_7H_{15}	58.5	—	(57)	88.5
C_6H_{13}	C_8H_{17}	54	(27)	66	90
C_7H_{15}	C_3H_7	57	—	—	93
C_7H_{15}	C_4H_9	50.5	—	—	97.5
C_7H_{15}	C_5H_{11}	42	—	—	92
C_7H_{15}	C_6H_{13}	51	—	51.5	96
C_7H_{15}	C_7H_{15}	54	—	66.5	92
C_7H_{15}	C_8H_{17}	57.5	—	76.5	94

( ) Monotropic transition temperature
[a] ΔH, 35.0 kJ mol^{-1}
[b] ΔH, 33.6 kJ mol^{-1}

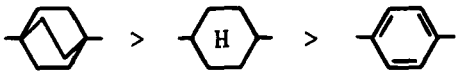
the dialkyl esters (V) and S_C and/or S_A phases in the case of the alkyl/alkoxy esters (VI).

The results in Tables III and IV demonstrate clearly that these novel bicyclo-octane esters ((V) and (VI)) constitute two new and interesting series of materials with strong nematic tendencies. The nematic temperature ranges are

wide, and in the case of the dialkyl esters (V), several of the homologues prepared are very low melting. The dialkyl ester (3/8) is a particularly good example, melting at 8°, and giving a nematic phase until 53°. Indeed, nine of the thirty-three dialkyl esters melt at 30° or below. The lowest melting alkyl/alkoxy ester (4/04) melts at 32.5° and remains nematic until 84.5°.

It is interesting to compare the liquid crystal properties of the new bicyclo-octane esters with those of the analogous benzoate esters and cyclohexane-1-carboxylate esters. Some typical data are recorded in Table V.

The melting points of these three different ester types are variable, but in some cases the bicyclo-octane ester can be the lowest melting. However, a consistent trend of decreasing T_{N-I} value for the esters is observed and may be represented as

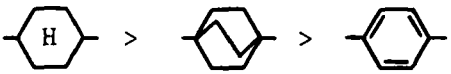


Because of the high T_{N-I} (agreeing with the general order quoted in the introduction) values and the variable behavior of the mps over the three series, the bicyclo-octane esters very often possess wider nematic temperature ranges than the analogous benzoates and cyclohexane-1-carboxylates. Indeed, when the melting point trends are most favorable, the wider range nematic phases for the bicyclo-octane esters not only persist until higher temperatures, but also commence at lower temperatures than do those for the other two ester systems. For example, for one particular homologue (with R, n-C_5H_{11}; R', OC_4H_9-n) of these three esters, the following results are obtained:

(1) benzoate ester—nematic range, 8.5° from 49°;
(2) cyclohexane ester—nematic range, 32° from 49°;
(3) bicyclo-octane ester—nematic range, 58° from 42°.

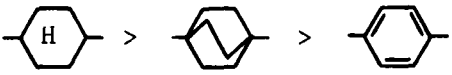
From the somewhat limited information available, the trends in smectic properties over the esters containing the three ring systems would appear to be:

(1) dialkyl esters



(for S_A/S_B phases)

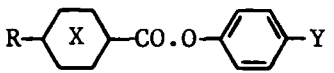
(2) alkyl/alkoxy esters

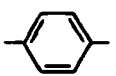
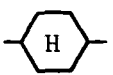
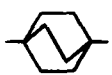


(for S_A/S_C phases)

TABLE V

Comparative transition temperatures (°C) for compounds of the general structure



X   

n-R	*n*-Y	C—N/I	N—I	C—S_C/N/I	S_C—S_A	S_A—N	N—I	C—S_A/N	S_A—N	N—I
C_3H_7	C_5H_{11}	14	20	32.5	—	—	34.5	29.5	—	55.5
C_5H_{11}	C_5H_{11}	26	35	36	—	(29)	48	31	—	64.5
C_3H_7	OC_4H_9	72	(59)	41.5	—	—	72.5	48	—	94
C_4H_9	OC_4H_9	47	(45)	38	—	—	68.5	32.5	—	84.5
C_4H_9	OC_6H_{13}	29	50	25	—	—	70	46	—	88
C_5H_{11}	OC_6H_{13}	36	59.5	23	25	38.5	78.5	54.5	—	97
C_7H_{15}	OC_6H_{13}	45.5	63	36	54	67.5	80	51	51.5	96

( ) Monotropic transition temperature

Two points should however be noted.

(1) The dialkyl bicyclo-octane esters exhibit S_B phases, whereas the corresponding cyclohexane esters exhibit S_A and/or S_C phases. Therefore, the comparison of the relative smectic tendencies for these two systems cannot be considered as strict.

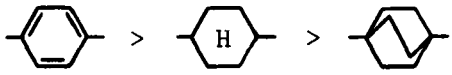
(2) In relation to the smectic orders for both the dialkyl and the alkyl/alkoxy series of esters, we should remember that no smectic phases have been recorded for the benzoate esters. Even an ester with two long terminal alkyl chains (9/9) is still purely nematic (C—N, 44.5°; N—I, (40°)).

PHYSICAL PROPERTIES

These two series of liquid crystalline esters containing the 1,4-disubstituted bicyclo(2.2.2)octane ring system, many of whose members are low melting and give good nematic ranges, have provided new nematic materials of potential for application in electro-optical display devices. The electro-optical and other physical properties of these bicyclo-octane esters have been studied by our colleagues at RSRE, Malvern, and their detailed results[13] on these and other related systems, were presented at the Kyoto Conference. However, the most significant features of their results for the bicyclo-octane esters ((V) and (VI)) may usefully be summarized briefly in the present context.

(1) The esters are colorless and of good thermal stability.

(2) Their smectic properties are not pronounced. In admixture with cyanobiphenyls, the dialkyl esters (V) show less pronounced injection of mono-layer, S_A phases than do the analogous benzoate and cyclohexanoate esters. For 60 wt % mixtures of each of the three dialkyl (5/5) ester types with 40 wt % of 4-cyano-4′-*n*-nonylbiphenyl (K27), the injected smectic properties lie in the following order based on the temperature for $T_{N-I} - T_{S_A-N}/T_{N-I}$:



(3) The dialkyl esters (V) have good mixing properties with one another and with cyanobiphenyls. A binary mixture (A) of two homologues (3/5 and 5/5) of the dialkyl bicyclo-octane esters possesses a low melting point (C—N, 5°) and a high clearing point (N—I, 58°).

(4) This simple mixture (A) exhibits a low birefringence (Δn, 0.075), a low dielectric anisotropy ($\Delta\epsilon$, −0.6), and a moderately low viscosity (η, 20°,

34 cP; 0°, 110 cP).

(5) A secondary mixture derived from cyanobiphenyls (60 wt %) and the mixture (A) (40 wt %) has a good sharpness in a twisted nematic cell ($M_{20°}$, 1.73) and a low temperature dependence of the threshold voltage ($1/V \cdot dV/dT$, 0.35% C^{-1}).

The physical properties and electro-optical responses of the alkyl/alkoxy bicyclo-octane esters (VI) in admixture with cyanobiphenyls are essentially similar to those of the dialkyl esters (V), except that the temperature dependence of threshold voltage is even *lower* ($1/V \cdot dV/dT$, 0.2%), although the viscosity is somewhat higher.

CONCLUSION

The two new series of esters ((V) and (VI)) containing the 1,4-disubstituted bicyclo(2.2.2)octane ring exhibit strong nematic character and are of moderate viscosity, low birefringence, and low dielectric anisotropy in the nematic phase. The clearing points of the esters are consistently higher than those of the corresponding benzoate and cyclohexanoate esters. The physical and electro-optical properties of these esters and their mixtures with, for example, cyanobiphenyls, give these esters real advantages for application in twisted nematic (and cholesteric-nematic phase-change) devices with multiplexed drive systems. The most significant features of mixtures of these esters with cyanobiphenyls are the good sharpness, and low temperature dependence of the threshold voltage, and the low tendency for injected smectic properties.

EXPERIMENTAL

Transition temperatures

The liquid crystal transition temperatures recorded in Tables III and IV were determined by optical microscopy using either a Nikon L-Ke polarising microscope or a Vickers M72c polarising microscope in conjunction with a Mettler FP52 heating stage and FP5 control unit. The Mettler stage could be cooled (<−20°) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage. In those instances when it was not possible to observe a liquid crystal transition directly, "virtual" nematic-isotropic liquid (N—I) transition temperatures were determined in the usual way.[3]

Spectral analysis

Infra-red, ^1H nmr and mass spectra were determined using, respectively, a Perkin Elmer 457 spectrometer, a Jeol JNM-4H 100 Mz spectrometer, and an AEI MS902 mass spectrometer.

Differential thermal analysis

Enthalpies of fusion of the most stable crystal forms of the esters ((V) and (VI)) were measured using a Stanton Redcroft (Model 671) low temperature differential thermal analyser (DTA). Indium was used as a standard for calibration, and the degree of error for the recorded enthalpy values is estimated at ±10%.

Structure and purity

Infra-red, ^{1}H nmr and mass spectra of the 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acids were obtained and compared with those of the known methyl and ethyl homologues previously reported by Holtz and Stock.[16] The spectra were found to be identical in all essential aspects. Combustion analyses (C and H) were obtained and the experimental results were found to be in good agreement with the required and calculated values—see Table VI.

The ^{1}H nmr, infra-red and mass spectra of the bicyclo-octane esters ((V) and (VI)) were consistent with the required structures, and each ester gave a single-spot on thin layer chromatography (tlc). Analysis of the esters by gas-liquid chromatography (glc) indicated purities of at least 99.0% and values of 99.9% were common.

Preparation of materials

The necessary 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acids were prepared from the known 1-*n*-alkyl-4-bromobicyclo(2.2.2)octanes[3] by a modified Koch-Haaf reaction. These acids were converted into the acyl chlorides in the

TABLE VI

Analytical data for the 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acids

Alkyl	Found (%) C	Found (%) H	Formula	Required (%) C	Required (%) H
Methyl*	71.3	9.6	$C_{10}H_{16}O_2$	71.4	9.6
Ethyl*	72.6	9.9	$C_{11}H_{18}O_2$	72.5	9.95
Propyl	73.4	10.4	$C_{12}H_{20}O_2$	73.4	10.3
Butyl	74.3	10.4	$C_{13}H_{22}O_2$	74.2	10.5
Pentyl	75.0	10.8	$C_{14}H_{24}O_2$	74.95	10.8
Hexyl	75.5	11.0	$C_{15}H_{26}O_2$	75.6	11.0
Heptyl	76.2	11.2	$C_{16}H_{28}O_2$	76.1	11.2
Octyl	76.7	11.3	$C_{17}H_{30}O_2$	76.6	11.35
Nonyl	77.2	11.5	$C_{18}H_{32}O_2$	77.1	11.5

* Calculated for (%) in the case of methyl and ethyl

normal way and interacted, without further purification, with the appropriate 4-*n*-alkylphenols and 4-*n*-alkoxyphenols using a modified literature method,[17] to yield the 4-*n*-alkylphenyl and 4-*n*-alkoxyphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates ((V) and (VI)). The esters were purified in the normal way by chromatography and subsequent distillation or crystallization.

The appropriate 4-*n*-alkylphenols and 4-*n*-alkoxyphenols were supplied by BDH Chemicals Limited (Poole), Dorset, UK, under a Supply Contract from the UK Ministry of Defense.

4-n-Alkylbicyclo(2.2.2)octane-1-carboxylic acids. Concentrated formic acid (98/100%, 30 cm^3) was added dropwise over a 6 h period to a vigorously stirred mixture of 1-*n*-alkyl-4-bromobicyclo(2.2.2)octane (0.0179 mol), anhydrous silver sulphate (0.0179 mol), and concentrated sulphuric acid (300 cm^3) initially cooled to 0° and maintained under anhydrous conditions.

The reaction mixture was then poured onto ice (800 g) and shaken for 20 min. The aqueous layer was decanted from inorganic solid and shaken with chloroform (3 × 200 cm^3). The combined organic layers were washed with dilute aqueous potassium carbonate (2 × 200 cm^3) and with water (2 × 1,000 cm^3), and then dried ($MgSO_4$). The crude 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylic acid was crystallized from methanol.

The results were: methyl, m/e, 168, 51%, mp 187–188° (lit 187–188°); ethyl, m/e, 182, 75%, mp 170–171° (lit 170–171°); propyl, m/e, 196, 65%, mp 213–214°; butyl, m/e, 210, 70%, mp 156–157°; pentyl, m/e, 224, 69%, mp 159–161°; hexyl, m/e, 238, 71%, mp 157–158°; heptyl, m/e, 252, 68%, mp 145–146°; octyl, m/e, 266, 73%, mp 126–127°; nonyl, m/e, 280, 76%, mp 130–131°. For analytical data see Table VI.

4-n-Alkylphenyl and 4-n-alkoxyphenyl 4-n-alkylbicyclo(2.2.2)octane-1-carboxylates ((V) and (VI)). A solution of either the 4-*n*-alkylphenol or 4-*n*-alkoxyphenol (0.0022 mol) in freshly-distilled, sieve-dried pyridine (5 cm^3) was added to a boiling solution of 4-*n*-alkylbicyclo(2.2.2)octan-1-oyl chloride (0.0022 mol)—prepared from the acid and thionyl chloride—in sodium-dried toluene (20 cm^3) under anhydrous conditions. The resultant solution was heated under reflux for 48 h, and then evaporated to dryness under vacuum. The residual, crude ester was taken up in a minimum volume of solvent and eluted through a column of silica-gel using a 2:1 (v/v) mixture of chloroform/light petroleum (bp 40–60°). Fractions giving a single-spot on tlc were combined and the products either crystallized (methanol or ethanol) or distilled (in a short-path distillation apparatus). The liquid crystal transition temperatures of the 4-*n*-alkylphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (V) and the 4-*n*-alkoxyphenyl 4-*n*-alkylbicyclo(2.2.2)octane-1-carboxylates (VI) are recorded in Tables III and IV respectively.

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References

1. G. W. Gray and S. M. Kelly, *J. Chem. Soc., Chem. Commun.*, 974 (1979).
2. G. W. Gray and S. M. Kelly, *Angew. Chem. Internat. Edn. Engl.*, in press.
3. G. W. Gray and S. M. Kelly, *J. Chem. Soc., Perkin II*, 26 (1981).
4. N. Carr, S. M. Kelly and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, in press; G. W. Gray, *Mol. Cryst. Liq. Cryst.*, in press.
5. G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.*, **9**, 130 (1973); *Pramana., Suppl.*, 381 (1975); *J. Chem. Soc., Chem. Commun.*, 431 (1974).
6. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem.*, **89**, 103 (1977); *Angew. Chem. Internat. Edn. Engl.*, **16**, 100 (1977); *Phys. Lett.*, **60A**, 421 (1977).
7. T. R. Criswell, D. J. Genova, R. T. Klingbiel and J. P. Van Meter, *J. Amer. Chem. Soc.*, **96**, 7651 (1974); D. Coates and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **37**, 249 (1976).
8. D. Demus, H-J. Deutscher, F. Kuschel and H. Schubert, *D.D.R. Patent*, **105**, 701 (1974); D. Demus, *Non Emissive Electro-optic Displays*, eds, A. R. Kmetz and F. K. Willison, Plenum Press, New York and London, p. 83 (1976).
9. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **53**, 147 (1979).
10. D. Bradshaw, E. P. Raynes and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, in press.
11. R. Steinsträsser, *Z. Naturforsch, Teil B*, **27**, 774 (1972).
12. T. Ishibashi, K. Odaware, H. Sakurada and K. Toriyama, *S.I.D. International Symposium*, Digest of Tech. Papers, p. 72 (1978).
13. J. Constant and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, in press.
14. G. W. Gray and S. M. Kelly, *J. Chem. Soc., Chem. Commun.*, 465 (1980).
15. T. Srithanratana, hitherto unpublished results.
16. H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, **86**, 5183 (1964).
17. M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).