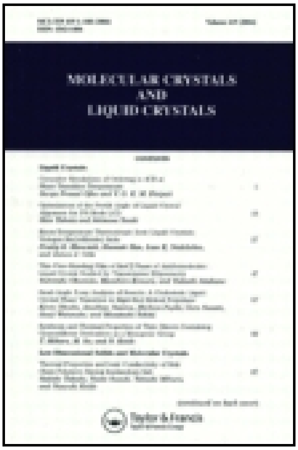

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A Comparison of the Properties of Some Liquid Crystal Materials Containing Benzene, Cyclohexane, and Bicyclo[2.2.2]octane Rings

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A Comparison of the Properties of Some Liquid Crystal Materials Containing Benzene, Cyclohexane, and Bicyclo[2.2.2]octane Rings

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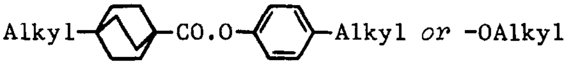
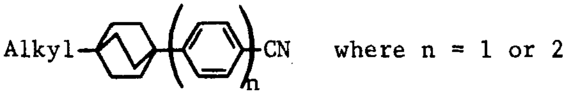
(*Received July 29, 1980*)

A preliminary study of the properties of nine cyanoaryl esters of various 4-alkylbicyclo[2.2.2] octane-1-carboxylic acids has been extended and results are now presented for a wider range of 4-cyanophenyl, 2-cyano-6-naphthyl, and 4-cyano-4′-biphenyl 4-alkylbicyclo[2.2.2.]octane-1-carboxylates.

These three types of ester, together with the esters and the cyano-compounds shown below





now make it possible to compare, over several systems, the effects on liquid crystal properties of replacing a 1,4-disubstituted benzene ring in a mesogen by (i) a *trans*-1,4-disubstituted cyclohexane ring, and (ii) a 1,4-disubstituted bicyclo[2.2.2]octane ring. The N-I transition temperatures for the majority of the homologues in these systems are consistently

bicyclo-octane > cyclohexane and benzene

Implications of these observations are discussed, and the properties of some further, new bicyclo-octane systems are considered in the light of these trends.

The bicyclo[2.2.2]octane ring was first used in the structures of compounds capable of forming liquid crystal phases by Dewar *et al.*[1] With reference to

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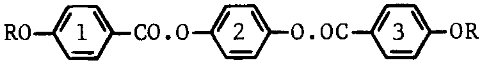
Paper presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

the fully aromatic tricyclic diesters (I), where RO = *n*-alkoxy



(I)

they replaced one, two, or all of the benzene rings (1 to 3) by 1,4-disubstituted bicyclo[2.2.2]octane rings (Ia). This alicyclic

(Ia)

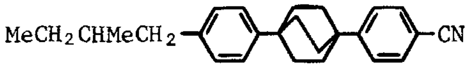
ring was chosen because it has a similar width to a benzene ring and because the 1,4-bonds are co-linear; the ring system is however thicker than the benzene ring.

It was argued that if ring geometry alone is important, these changes in structure should not affect T_{N-I} greatly. Although T_{N-I} fell by only 28° on replacing only ring 2, replacement of rings 1 and/or 3 had a large effect, *ca* 76° per ring, and approximately additive. Dewar *et al.*[1] concluded that use of the bicyclo-octane (BCO) ring reduces both the content of polarisable π-electrons and the extent of conjugative interactions in the molecules, thereby reducing the anisotropy of molecular polarisability and consequently T_{N-I}.

However, these authors[1] stressed that the geometric role of a ring system is very important, because replacement of ring 2 in (I) by a *trans*-1,4-disubstituted cyclohexane ring gave, with RO = MeO, a monotropic nematic phase corresponding to a decrease in T_{N-I} of 75° compared with the BCO analogue and of 103° compared with the fully aromatic compound (I). They concluded that a rigid ring geometry is essential.

These results led us to incorporate the BCO ring (Ia) in the structures of some simpler systems such as the 4-alkoxy-4′-cyanobiphenyls and 4-alkyl-4″-cyano-*p*-terphenyls which had been shown to be of value in commercial display systems. We first examined 1-(4′-cyanophenyl)-4-*n*-pentyloxybicyclo[2.2.2]octane (II) and 1-(4′-cyanophenyl)-4-(4′-(2″-methylbutyl)phenyl)bicyclo[2.2.2]octane (III).

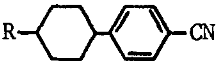
(II)



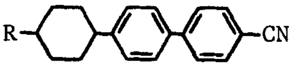
(III)

Discouraging results were obtained, especially for (II)[2] which melted at over 50°. No nematic phase was formed on heating or cooling, and studies of mixtures showed that the compound had a virtual T_{N-I} well below room temperature. Compound (III)[3] melted 20° higher and had a T_{Ch-I} 50° lower than the corresponding fully aromatic terphenyl analogue.

At about this time, the group at Merck[4] published their results on compounds of structure (IV) and (V), the now well known PCH and BICH materials respectively. The compounds had very good T_{N-I} values, despite the *trans*-1,4-disubstituted cyclohexane rings. Thus, compound (IV), R = n-C_5H_{11} had a T_{N-I} 20° *higher* than that of the



(IV)



(V)

analogous biphenyl, and for compound (V), R = n-C_5H_{11}, T_{N-I} was only 20° lower than that of the analogous p-terphenyl.

However, it seemed significant that no reports were made of nematic properties for compounds of the type (IV) and (V) where R = alkoxy. This was related to the fact that the large decreases in T_{N-I} observed[1] when terminal rings 1 and/or 3 were replaced in (I) by the BCO ring system were associated with materials in which a *methoxy* group is directly linked to the BCO ring. If alkoxy groups directly linked to alicyclic rings are in fact unfavourable to nematic properties, this would explain these facts, including the poor result obtained with the pentyloxy compound (II).

We decided therefore to prepare one compound of type (VI) with an alkyl group on the BCO ring

(VI)

The first compound made, with $n = 5$, 1-(4′-cyanophenyl)-4-n-pentylbicyclo[2.2.2]octane had C–N, 62°; N–I, 100°.

Relative to the systems (VI) where the BCO ring is replaced by (a) a benzene ring (K15), T_{N-I} has been increased by 65°, (b) a cyclohexane ring (PCH5), T_{N-I} has been increased by 45°.

Eventually we showed[5] that these large increases in T_{N-I} occurred for all the homologues from $n = 3$ to 9. Only for $n = 1$ and 2 are the T_{N-I} values for the BCO compounds lower than those of the biphenyls, and this is connected with the fact that the T_{N-I} curves initially rise very steeply for the BCO series (Figure 1), but *fall* initially for the biphenyl series. These general results show that for most of the homologous series, the order of T_{N-I} is

BCO > Cyclohexane > Benzene (Order 1)

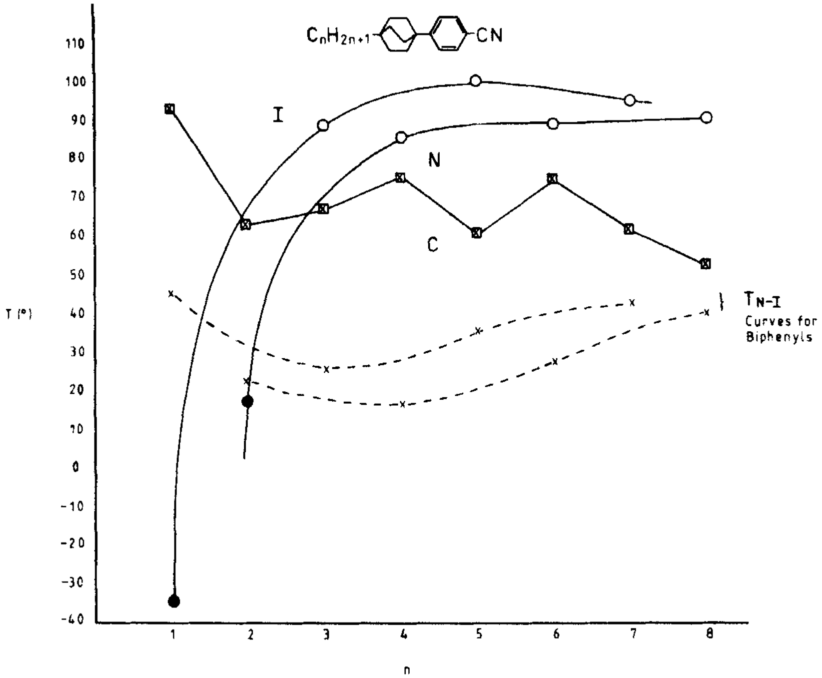
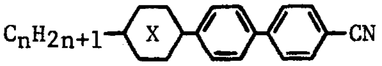


FIGURE 1 Plot of transition temperatures against chain length: ○ nematic-isotropic liquid; ☒ crystal-nematic or isotropic liquid; ● isotropic liquid-virtual nematic. × nematic-isotropic transition points for the related 4-alkyl-4′-cyanobiphenyls.

For the terphenyl analogues (VII), an inversion of order 1 in the last two cases was observed on changing ring X from BCO to cyclohexane to benzene



(VII)

The order of decreasing T_{N-I} was

BCO > Benzene > Cyclohexane (Order 2)

To establish whether these results applied to a wider range of systems, we have prepared some other BCO compounds, starting with cyanoaryl esters derived from 4-alkylbicyclo[2.2.2]octane-1-carboxylic acids. Preliminary results for a few of these esters have been published in a short communication.[6] Fuller results are now given in Tables I, II, and III. The

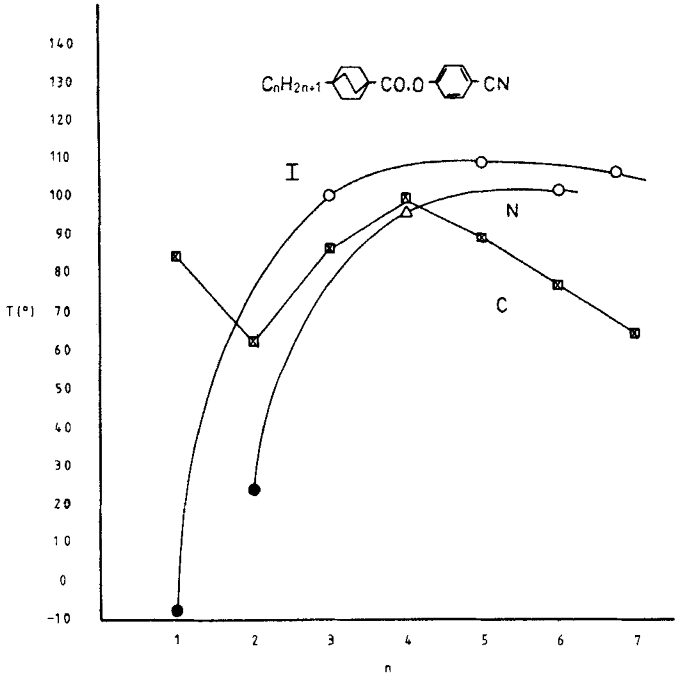
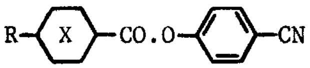
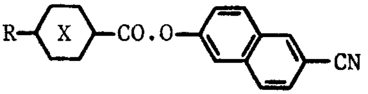


FIGURE 2 Plot of transition temperatures against chain length: ○ nematic-isotropic liquid; ☒ crystal-nematic or isotropic liquid; ● isotropic liquid-virtual nematic; △ monotropic nematic-isotropic liquid.

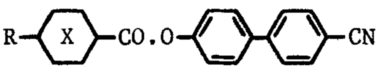
structure types are



(VIII)



(IX)



(X)

and the data tabulated refer to the cases where ring X is a BCO ring.

The results in Table I are plotted against the number of carbon atoms in the *n*-alkyl group (R) in Figure 2. As in the case of Figure 1, a very sudden rise in T_{N-I} occurs on passing from the homologues with $n = 1$ or 2 to those

TABLE I

Data for esters of structure (VIII)—ring X = BCO; R = *n*-alkyl

R	C–N/I (°)	N–I (°)
CH_3	84	[−8]
C_2H_5	62	[23.5]
C_3H_7	86.5	100
C_4H_9	99	(96)
C_5H_{11}	89	109
C_6H_{13}	77	102
C_7H_{15}	54	106

[ ] = virtual transition temperature
( ) = monotropic transition temperature.

TABLE II

Data for esters of structure (IX)—ring X = BCO; R = *n*-alkyl

R	C–N/I (°)	N–I (°)
CH_3	147.5	[81]
C_2H_5	137	146
C_3H_7	134.5	201
C_4H_9	108	202
C_5H_{11}	106	204
C_6H_{13}	98	204
C_7H_{15}	92.5	190

[ ] = virtual transition temperature

TABLE III

Data for esters of structure (X)—ring X = BCO; R = *n*-alkyl

R	C–N/S_A (°)	S_A–N (°)	N–I (°)
CH_3	162.5	—	198
C_2H_5	137	—	244
C_3H_7	142	—	289.5
C_4H_9	143	—	285.5
C_5H_{11}	143.5	—	282.5
C_6H_{13}	134	—	270
C_7H_{15}	135.5	180.5	263.5

with longer alkyl chains. In making comparisons with related series of esters for which the T_{N-I} curves have a very different shape, eg, falling steeply from $n = 1$ or 2, erroneous conclusions may be reached about the behaviour of higher homologues based on the properties of the methyl and ethyl derivatives.

Considering the data in Table I, it is clear that the BCO esters melt somewhat higher (25–30°) than the analogous esters derived from 4-alkylbenzoic or *trans*-4-alkylcyclohexane-1-carboxylic acids, but have much higher T_{N-I} values. Similar conclusions arise from the data in Tables II and III, and the position is summarised using average T_{N-I} values in Table IV.

TABLE IV

Comparative data on T_{N-I} values for esters (VIII), (IX), and (X)

Ring X =	BCO	Cyclohexane	Benzene
Average T_{N-I} *for*			
(VIII), $n = 4$ to 7	103°	75°	51°
(IX), $n = 3$ to 7	200	166	146
(X), $n = 4$ to 7	275.4	234.4	233.5

The order of decreasing T_{N-I} for esters of types (VIII) and (IX) is

$$\text{BCO} > \text{Cyclohexane} > \text{Benzene}$$

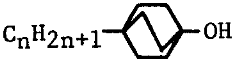
but for the esters (X), it is somewhat modified to

$$\text{BCO} > \text{Cyclohexane} \approx \text{Benzene}$$

In the case of the esters (X), we are approaching the Order 2 obtained for the terphenyl type systems (VII), for which high T_{N-I} values are involved. The T_{N-I} values for the esters (X) are in fact higher than those of the terphenyl analogues (VII), and although the T_{N-I} values for the cyclohexane and benzene systems are very close, an inversion in the order does not in fact occur. Although this denies a *consistent* trend in the order with increasing T_{N-I}, it would appear that the cyclohexane ring is less advantageous relative to benzene when high T_{N-I} values are involved, and we have already discussed[7] this in terms of the possible adoption at high temperatures of cyclohexane conformations unfavourable to the nematic order.

However, the fact remains that for a total of five different systems ((VI) to (X)), the T_{N-I} values of BCO systems are superior to those of the analogous compounds containing a cyclohexane or a benzene ring.

Furthermore, at Bordeaux, a paper was presented by Gayvandov and Kovshev[8] on esters derived from 4-alkylbicyclo[2.2.2]octan-1-ols (XI). This work showed apparently that they had observed some increases and some



(XI)

decreases in T_{N-I} on replacing benzene rings by BCO rings.

This encouraged us to look at a still wider variety of materials to check the general applicability of the order BCO > Cyclohexane or Benzene for T_{N-I}. A further reason for doing this was the hope of producing some BCO derivatives with low melting points. Coupled with their high T_{N-I} values, the materials would then have extremely good nematic thermal ranges. A further incentive was that we had some evidence that the BCO ring causes interesting changes in the elastic properties of nematic phases, and that advantage might be taken of this in commercial applications of these materials. Such aspects are discussed in other papers[9–11] to be presented at this meeting.

The results of our studies to date are summarised in Table V. Although some of the systems listed in Table V are the subject of full papers presented at this meeting, in other cases, the work is still incomplete, and full details must await future publications. However, the information summarised is sufficient to show the trends which occur for T_{N-I}. To simplify the data, T_{N-I} values are quoted for single, selected homologues, but in those cases where it is possible to check, the conclusions are substantiated for a range of homologues.

This extends to seventeen different systems, the range of materials for which the BCO ring system gives higher T_{N-I} values than those for the analogous materials with a cyclohexane or a benzene ring. Comparisons cannot be made over all three types in all cases, but we now have eleven systems for which the order of decreasing T_{N-I} is clearly

BCO > Cyclohexane > Benzene

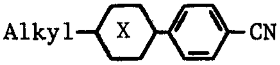
There are of course some known exceptions to the order cyclohexane > benzene. Two instances have already been mentioned where fairly high T_{N-I} values are concerned. In addition, the simple 4-alkylbenzoic acids and *trans*-4-alkylcyclohexane-1-carboxylic acids show an inversion of this order, T_{N-I} for the benzoic acids being higher than T_{N-I} for the cyclohexane acids, eg, for alkyl = C_6H_{13}, the T_{N-I} values are 115° and 96.4°, respectively. Here the T_{N-I} values are not very high, but of course we are now comparing two systems of a rather special kind, for the liquid crystal properties depend on the hydrogen-bonded dimers formed by the acids, as well as on the rest of the molecular structure. In the case of the now known 4-alkylbicyclo[2.2.2]-octane-1-carboxylic acids, the m.p.s. are quite high, and the melts do not supercool enough to allow mesophase formation. For example, with alkyl = C_6H_{13}, the C–I value is 157–8° (recrystallisation occurring at *ca* 147°), and in the basence of virtual T_{N-I} values, we cannot say where these acids would lie in the order of T_{N-I} values.†

Other exceptions to the cyclohexane > benzene order have been reported by Soman.[20] These systems have however rather special features in that in the benzene systems a substituent RNH— group carrying a lone pair of electrons is attached to the aromatic ring. Strong conjugative interactions possible in the benzene analogue cannot therefore occur in the cyclohexane system, and we have a position similar to that of having a group RO— linked to a cyclohexane or BCO ring. These cases merit careful consideration, and they have been discussed separately.[21]

Although we must remember that such exceptions do occur and that subtle influences may be at work in these cases, it is interesting to reflect on the now numerous systems for which T_{N-I} is in the order

BCO > Cyclohexane > Benzene

From theoretical considerations, the implication would be that the anistotropy of molecular polarisability ($\Delta\alpha$) must decrease in the same order. Intuitively, an organic chemist would say that this would not be the case, and recent experimental results obtained by Dunmur and Tomes[22] on the systems (XXIV)‡

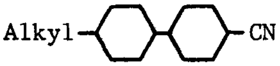


(XXIV)

show that the order of decreasing $\Delta\alpha$ is

X = Benzene > BCO > Cyclohexane‡

As might be expected, $\Delta\alpha$ for the CCH compounds (XXV) is the lowest of all



(XXV)

Therefore, the *order* of T_{N-I} does not appear to be *determined* by the order of anisotropy of molecular polarisability. Nor is this order determined by the isotropic molecular polarisabilities.[22] One is forced to conclude that other factors must play a part, and although a firm explanation of the order cannot be given, it is possible that repulsive interactions may be a key factor. For example, repulsive interactions between alicyclic rings and neighbouring

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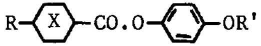
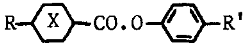
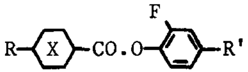
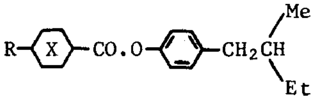
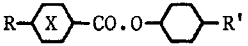
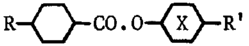
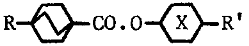
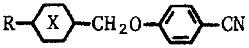
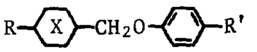
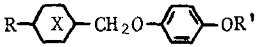
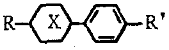
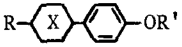
† Range of C–I values from alkyl = methyl to *n*-heptyl = 213 to 145°.

‡ Since this was written, the results referred to[22] have been confirmed by data presented[23] at this meeting.

TABLE V

Comparative data for some other systems (R, R′ = *n*-alkyl)† containing bicylo-octaine, cyclohexane, or benzene rings.

Structure	Code No	X =	T_{N-I} (°)*			Ref
			BCO	Cyclohexane	Benzene	
	XII		93.5	70	51.9	9; 12; 13
	XIII		61.5	48	26	9; 12; 13
	XIV		62	36.5	(1)	9; 14; 14
	XV		28	(7)	(−1)	9; 14; 14
	XVI		$[92]^{**}$	52.1^{a}	-	15; 16; -
	XVII		92^{a}	52.1^{a}	$(43)^{a}$	15; 16; 12
	XVIII		$[126]^{**}$	$[92]^{**}$	61.5	15; 15; 9
	XIX		73	(48.6)	-	15; 17; -

	XX	[26]^b	[17]^b	-	15; 15; -
	XXI	[64]^c	(50)^c	-	15; 15; -
	XXII	[31]^a	(<-30)^e	††	15; 18; 19
	XXIII	85.7^d	(30-40)^e	S_B/S_E	15; 18; 19

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* ( ) monotropic; [ ] virtual

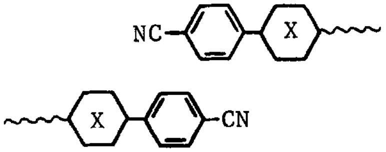
† unless otherwise indicated below, R' and/or R = n-C_5H_{11}

a R = C_5H_{11}; R' = C_3H_7
b R = C_5H_{11}; R' = CH_3
c R = C_5H_{11}; R' = C_4H_9
d R = C_5H_{11}; R' = C_2H_5
e preliminary data (averaged for several homologues)

†† No phases or plastic crystals

** This compound is smectic giving a smectic-isotropic transition; however, to make comparisons possible with other T_{N-I} values, a virtual T_{N-I} value has been obtained from the properties of a range of mixtures of the compound with a nematogenic system (E7) which strongly represses the smectic properties. A mixture of the ester containing only 10 wt % of E7 is nematic, and the virtual T_{N-I} is only a few degrees lower than the enantiotropic T_{S-I} value, when one ring is cyclohexane.

dipolar functions or aromatic ring systems may be smaller than for the aromatic analogues and consequently less disruptive of the nematic order. Thus we know[24] that in all of the systems (XXIV), there is evidence in the *nematic* phases for molecular pairing of the type shown below and which accounts for—amongst other things—the interdigitated bilayer structure of the S_A phase of the cyanobiphenyls (X = benzene in (XXIV)).



As can be seen, the polar CN group tends to be near ring X whose nature could markedly influence the attractive or repulsive situation.

Steric factors, ie, the ability of the molecules to pack together well in the nematic "lattice" may also be important, and in this context, the greater bulk of the BCO and cyclohexane rings must be considered because of their effect on molecular shape and volume and the significance of this in relation to models for the nematic phase based on hard-rod theories.

Finally, molecular flexibility is a consideration, for whereas the BCO ring is rigid, the cyclohexane ring is not, and this may contribute to the lower T_{N-I} values of the cyclohexane systems.

Therefore, although the results of these studies of cyclohexane and BCO systems cannot be said to be understood in theoretical terms, they are important in educating us to be cautious about over-generalising on the basis of currently accepted theories. Theories are only as sound as the experimental basis of fact on which they rest, and as new experimental observations are made, the theories must develop and be modified.

Finally some comment should be made on the relative smectic behaviour of the various systems that have been discussed in this paper.

In fact, no clear pattern emerges even over the systems for which the order of T_{N-I} is clearly

BCO > Cyclohexane > Benzene

There are a number of contributory factors to this situation.

1 For some systems, long chain homologues have not yet been studied.

2 For other systems for which long chain homologues have been made, no smectic properties have been observed.

3 For some systems, existing data are complicated by variations in the smectic phase types exhibited.

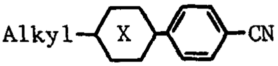
In the case of the cyanoaryl esters reported in this paper, the only available transition temperatures involving smectic phases are the T_{S_A-N} values for the three ester types of structure (X)—Table III. The values are

	X = Benzene	Cyclohexane	BCO
T_{S_A-N} (°) − C_7	<92	179	180.5
C_8	183	—	—

The order of smectic A thermal stability would therefore appear to be

BCO ≈ Cyclohexane > Benzene

However, for the system



no smectic phases have been found up to alkyl = C_9 for X = cyclohexane or BCO, and the order of S_A thermal stability is now

Benzene > BCO or Cyclohexane

For the dialkyl esters (XIII), no smectic phases have been reported for X = benzene, but late in the cyclohexane and BCO series, S_A and S_B properties respectively do occur. This makes the order

Cyclohexane > BCO > Benzene

For the alkyl alkoxy esters (XII), the benzoate esters again have no established smectic properties, whereas the BCO and cyclohexane esters with long alkyl chains have S_A and S_C properties, the order again being

Cyclohexane > BCO > Benzene

Then again, for the simple systems (XXIII)—see Table V—the order is

Benzene > BCO or Cyclohexane

whereas for the esters (XVI), the BCO compound is a pure smectogen, and the cyclohexane and benzene analogues are pure nematogens. With this variety of smectic orders, one can only make two general remarks:

1) When the smectic properties of BCO and cyclohexane systems are more pronounced than those of the benzene analogues, this occurs in systems for which no smectic properties have been observed in the benzene systems. Thus the smectic properties of the BCO and cyclohexane systems are usually quite strongly repressed (except for (XVI)), and occur only when combinations of quite long alkyl chains are used.

2) In other systems where the benzene compounds show smectic properties

or are even totally smectic, only nematic properties have so far been found for the BCO and cyclohexane analogues.

EXPERIMENTAL

Materials The preparation of the 4-alkylbicyclo[2.2.2]octane-1-carboxylic acids has already been described,[25] and the cyanoaryl esters were made from these acids by a routine esterification procedure. The preparations of other materials referred to in Table V have either been described elsewhere[14] or will be reported in future publications. All materials for which thermodynamic data have been reported have given satisfactory results on elemental analysis, and have had their structures and/or purities checked by normal procedures (infra-red spectroscopy, mass spectrometry, n.m.r. spectroscopy, thin layer chromatography, and g.l.c.).

Transition temperatures were measured by optical microscopy (Nikon LKe polarising microscope) in conjunction with a Mettler heated stage (FP 52) and temperature control unit (FP 5). Where necessary, data were confirmed by D.T.A. (Stanton Redcroft Low Temperature Thermal Analyser, Model 671B).

Note: Since this manuscript was completed, some new results on cyanoaryl esters have been obtained and are summarised below:

Structure (VIII) (Table I), R = C_8H_{17}; C–N, 59°; N–I 98°
Structure (IX) (Table II), R = C_8H_{17}; C–S_A, 91°; S_A–N, 129°; N–I, 180°
Structure (X) (Table III), R = C_8H_{17}; C–S_A, 126°; S_A–N, 199°; N–I, 254°

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