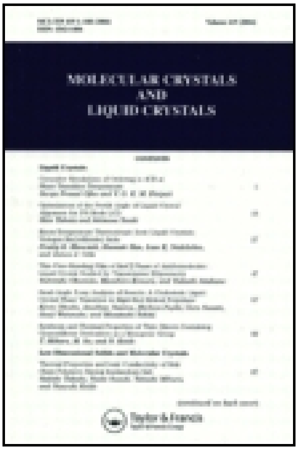

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The Preparation of 1,4-Di-n-alkyl-and 1-n-Alkyl-4-n-alkoxybicyclo-(2.2.2)octanes, and 1-n-Alkyl-4-n-alkoxybicyclo(2.2.2)octan-2-ones and and Investigation of Their Viscosities and T_{N-1} Values

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The Preparation of 1,4-Di-n-alkyl- and 1-n-Alkyl-4-n-alkoxybicyclo-(2.2.2)octanes, and 1-n-Alkyl-4-n-alkoxybicyclo(2.2.2)octan-2-ones and an Investigation of Their Viscosities and T_{N-I} Values†

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(*Received October 8, 1984*)

Several 1,4-di-n-alkylbicyclo(2.2.2)octanes ((4), dialkyl BCO) have been prepared and virtual T_{N-I} values and extrapolated viscosities are reported. Their T_{N-I} values are markedly dependent on the nature of the host, but the ability of the BCO unit to give derivatives of relatively high T_{N-I} is confirmed; the viscosities of the dialkyl BCO derivatives in various host mixtures are given and compared with the values for other low viscosity additives. 1-n-Alkyl-4-n-alkoxybicyclo(2.2.2)octanes and 1-n-alkyl-4-n-alkoxybicyclo(2.2.2)octan-2-ones, (5) and (6) respectively, have also been prepared and the effect of the ether and carbonyl functions on the T_{N-I} values is discussed. An outline of the synthetic routes to (4), (5) and (6) is given.

INTRODUCTION

All electro-optical display devices which use a nematic or a cholesteric phase require mixtures of low viscosity so that fast rise and decay times can be achieved and so that the device can be usefully operated at low temperatures. Ideally, the nematogens themselves should be of as low a viscosity as possible, but, if their viscosity is insufficiently

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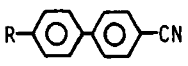
†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

low, then a low viscosity additive can be used in mixtures with the more viscous material of higher T_{N-I} value.

The compounds first used successfully in twisted nematic displays were the 4-n-alkyl-4′-cyanobiphenyls (K series) (1). Subsequently the cyclohexane (CH) and bicyclo(2.2.2)octane (BCO) derivatives ((2) and (3) respectively) were shown to have even higher T_{N-I} values (e.g., for R = n-C_5H_{11} the T_{N-I} values for (1), (2), and (3) are 35°, 55°, and 100°C respectively) and in many other systems also the bicyclo(2.2.2)octane > cyclohexane > benzene order of decreasing T_{N-I} values has been noted.[1]



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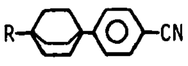

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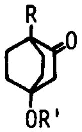
Because 1,4-disubstituted bicyclo(2.2.2)octane has the ability to generate nematic mesophases of high thermal stability it would apparently offer the greatest opportunity for providing simple molecules of small molecular size, so favouring a low viscosity, and yet maintaining T_{N-I} values as high as possible. We have therefore prepared a series of 1,4-di-n-alkylbicyclo(2.2.2)octanes (4) and 1-n-alkyl-4-n-alkoxybicyclo(2.2.2)octanes (5) and measured their virtual T_{N-I} values and extrapolated viscosities. In this paper we report the synthetic routes to these compounds and we compare their T_{N-I} values and their viscosities; we also comment briefly on the results for compounds (6), which are precursors to (5).

(4)

(5)



(6)

R,R' = n-alkyl

DISCUSSION

1,4-Di-n-alkylbicyclo(2.2.2)octanes (4)

The virtual T_{N-I} values and the extrapolated viscosities for the alkyl and dialkyl compounds are given in Table I. All of these compounds are isotropic liquids at room temperature and for a given material a

TABLE I

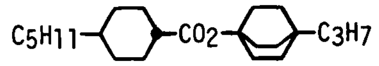
Virtual T_{N-I} values and extrapolated viscosities (η) for 1,4-di-n-alkylbicyclo(2.2.2)octanes (4)

	R	R′	T_{N-I} (°C)	η at 20°C[a] (cP)	η at 0°C[a] (cP)
BCO 50	C_5H_{11}	H	$-97^{a,g}$ $-149^{b,e}$	Segregation occurs[b]	
BCO 51	C_5H_{11}	CH_3	$-106^{a,f}$ $-136^{b,e}$		
BCO 53	C_5H_{11}	C_3H_7	$-77^{b,e}$		
BCO 55	C_5H_{11}	C_5H_{11}	$-18^{a,h}$ $-36^{b,e}$ $-47^{c,f}$ $-57^{d,e}$	7.7	20.2
BCO 57	C_5H_{11}	C_7H_{15}	$-30^{b,e}$	8.4	22.2
BCO 32	C_3H_7	C_2H_5	$-147^{b,e}$	Segregation occurs[b]	

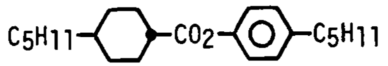
Nematic hosts a . . . E7, b . . . ZLI 1132, c . . . 5HEB3, d . . . 5HE5
Maximum % by weight of test compound e . . . 20%, f . . . 25%, g . . . 30%, h . . . 50%

[a] Extrapolated from data for 20% by weight mixtures in ZLI 1132
[b] Mixtures segregated to various extents on standing

5HEB3 .....



5HE5 .....



wide range of virtual T_{N-I} values was obtained depending upon the host which was used for the measurement. The T_{N-I} values for the BCO 50, 51 and 55 compounds were measured using E7 and ZLI 1132, and each compound gave a lower T_{N-I} value from the ZLI 1132 mixture. The values obtained using ZLI 1132 as host may possibly be the more reliable, as the virtual T_{N-I} value for BCO 50 is lower than that for BCO 51. Also, as we progress from BCO 51 through to BCO 57, maintaining one alkyl group at pentyl and lengthening the other for odd members, the virtual T_{N-I} values from ZLI 1132 rise steeply at first and then level off in a manner (Figure 1) consistent with that found for a number of homologous series.

However, it must be noted that the dialkylbicyclo(2.2.2)octanes are non-polar compounds of low dielectric anisotropy, whereas E7 and ZLI 1132 contain polarisable aromatic systems, have relatively high positive values of dielectric anisotropy, and each host consists of cyano-substituted molecules that can give an antiparallel pairwise

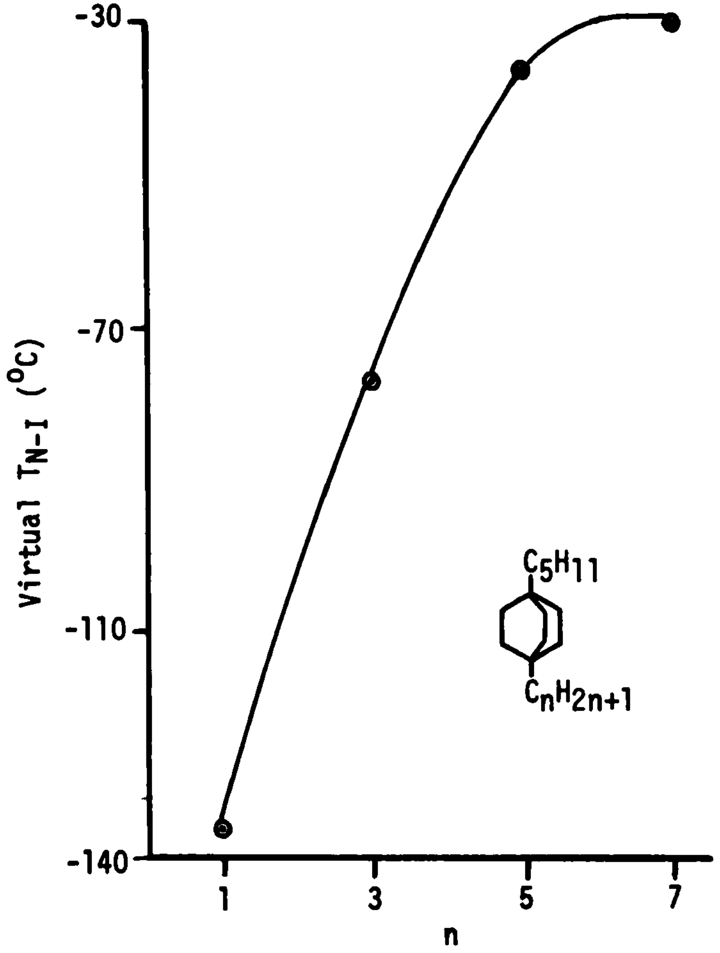


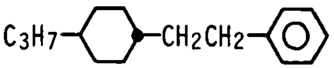
FIGURE 1 Plot of virtual transition temperatures (T_{N-I}) against number (n) of carbon atoms in the alkyl group of the 1-n-alkyl-4-n-pentylbicyclo(2.2.2)octanes.

correlation. We therefore examined some mixtures of BCO 55 in host systems which do not show pairwise correlation and are structurally more similar to the additive, i.e., the 5HEB3 and 5HE5 compounds (see Table I), but even *lower* virtual T_{N-I} values were obtained. It therefore appears that the dialkyl compounds more effectively disrupt the inter-molecular order in the nematic phase of the ester hosts which are, like the dialkyl compounds, mainly composed of saturated units, whereas they are less effective in influencing the anti-parallel arrangements in cyano-aromatic systems, particularly the biphenyls with their fully aromatic core. Such variations in virtual T_{N-I} values emphasise strongly the hazards in obtaining virtual T_{N-I} values which permit comparison between the results for other compounds obtained using different hosts. Eidenschink also has provided results which show a difference in virtual clearing point for lauronitrile [$CH_3(CH_2)_{10}CN$] of 190°C depending upon the host[2] and Schad and Osman have discussed the deviations from ideal behaviour seen in polar-non-polar binary systems.[3]

It can however be concluded that for compounds which contain a single cyclic unit and are fully saturated, the 1,4-di-n-alkylbicyclo(2.2.2)octanes have quite high T_{N-I} values, indicating again that the BCO unit is a good system for promoting nematic behaviour. 1,4-Dipentylbenzene was prepared in order to compare the benzene and BCO unit in these simple systems and it had a virtual T_{N-I} value of −175°C (from up to 20% by weight mixtures in E7); due to segregation shown by mixtures of this compound with ZLI 1132, a virtual value could not be obtained for this host. The virtual value in E7 is 157°C lower than that of the BCO analogue. Although effects dependent upon the nature of the host and the solute may again be at work, the magnitude of this difference would appear further to illustrate the ability of the BCO unit to enhance nematic thermal stability.

The viscosity measurements were carried out at 20°C and 0°C, but many of these mixtures involving the compounds of shorter alkyl chain length showed clear segregation and only the results for the 5/5 and 5/7 compounds were realistic and give a consistent change in viscosity with chain length and temperature.

Further investigations of the properties of some of these compounds have been carried out at R.S.R.E. (Malvern) using a host which gave no segregation problems. These gave consistent results and enabled a better comparison to be made with the results for (7) (PECH 30) and (8) (PCH 32) which are compounds of low viscosity; see Table II. The trends in viscosity in relation to structure and with variation of temperature are now consistent. The viscosities of the mixtures containing 1,4-dialkylbicyclo(2.2.2)octanes and PECH 30 are very similar, but they are higher than those of a mixture containing PCH



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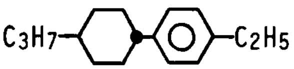


(8)

TABLE II[a]

Viscosities (η) and T_{N-I} values of a 27% by weight mixture of several hydrocarbons in a standard host

Compound	η (cP) 20°C	η (cP) 0°C	T_{N-I} (°C)
BCO 53 (4)	21	63	79
BCO 55 (4)	22	68	86
BCO 57 (4)	24	72	82
PECH 30 (7)	22	64	72
PCH 32 (8)	19	53	86.5

[a] We gratefully acknowledge these results which were provided by J. Constant and E. P. Raynes (RSRE, Malvern).

32. The T_{N-I} values for mixtures containing the BCO compounds have a slightly different trend from that shown in Table I, but all are higher than that for PECH 30, and the mixture containing BCO 55 has a T_{N-I} value almost equal to that of the PCH 32 mixture. These results indicate that BCO 55 is not markedly inferior to PCH 32.

E. Merck (Darmstadt, FRG) have also compared the T_{N-I} values, viscosities, and other physical properties of mixtures containing PCH 32 or dialkyl BCOs and some results which allow comparison of BCO 55 and PCH 32 are given in Table III. These results substantiate the conclusion that PCH 32 and BCO 55 have similar T_{N-I} values and similar viscosities. In addition, the fully saturated additive (BCO 55) has, as expected, reduced the birefringence of the mixture, and has increased the permittivity, presumably by diminishing the anti-parallel correlation in the cyano host. E. Merck have also shown that

TABLE III[a]

Comparison of some physical properties of PCH 32 and BCO 55

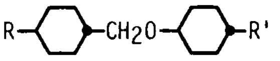
		Host + 10% PCH 32	Host + 10% BCO 55
T_{N-I} (°C)		85	84
η (cP)	20°C	18	18
	0°C	48	51
	−20°C	210	240
	−30°C	610	660
Δn		0.13	0.12
$\Delta\epsilon$		3.5	4.0

[a] We gratefully acknowledge these results which were provided by Dr. B. S. Scheuble (E. Merck, Darmstadt).

the vapour pressure of BCO 53 (molecular weight 222) is significantly greater than that of PCH 32 (molecular weight 230); BCO 53 would therefore be less suitable for electro-optical cells filled under reduced pressure.

1-n-Alkyl-4-n-alkoxybicyclo(2.2.2)octanes

Four compounds of this series were prepared and their virtual T_{N-I} values (see Table IV) are approximately 50° *lower* than those for the analogous dialkyl compounds. This reduction in T_{N-I} probably arises because the ether function produces a dipole acting across the molecular long axis which reduces the thermal stability of a nematic phase, whereas in an alkyl aryl ether the conjugation of the ether oxygen with the aromatic system is a favourable factor.[1,4] The effect of an ether group adjacent to an alicyclic ring in a fully saturated system (9) has also been reported by Osman.[5] He commented that the presence of the ether group in compound (9) produced nematogens with melting points and T_{N-I} values (e.g., for (9), $R = R' = n—C_3H_7$, T_{N-I} is 17.5°C) which are lower than those for the corresponding esters in which the central —CH_2O— group is replaced by —CO.O— (the T_{N-I} value for the corresponding ester is 36.6°C). What is also of interest is that hydrocarbon (10) ($R = R' = C_3H_7$),



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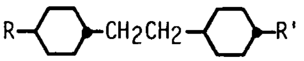


(10)

TABLE IV

Virtual T_{N-I} values of 1-n-alkyl-4-n-alkoxybicyclo(2.2.2)octanes (5) and 1-n-alkyl-4-n-alkoxybicyclo(2.2.2)octan-2-ones (6)

Substituents R	OR'	(5) T_{N-I}^a (°C)	(6) T_{N-I}^b (°C)
C_3H_7	OC_4H_9	−115	−105
C_5H_{11}	OC_4H_9	−92	−75
C_7H_{15}	OC_4H_9	−85	−86
C_3H_7	OC_2H_5	−163	−163

Nematic host is ZLI 1132

[a]. . . up to 25% by weight mixtures
[b]. . . up to 20% by weight mixtures

although strongly smectic in character ($T_{S_B\text{-}I}$ is 71.5°C), has a virtual T_{N-I} value of 60°C[6] and therefore the T_{N-I} value of the analogous ether is more than 40°C lower than that of the hydrocarbon; the effect of replacing methylene by oxygen is therefore similar in both of these saturated systems.

The effect of incorporating an oxygen atom at different positions in the alkyl chain of 4-butyl-4'-cyanobiphenyl (11a) is illustrated by the values given below. With the oxygen adjacent to the aromatic system (11b) a large increase in T_{N-I} is produced, but with the oxygen isolated from the aromatic system (11c), a decrease of approximately 20°C occurs. The effect is qualitatively the same as in compounds (5) and (9), but the additional factor of anti-parallel correlation in the cyanobiphenyls may be responsible for diminishing the influence of the oxygen atom.

(11)

	T_{N-I} (°C)
a, X = $CH_3CH_2CH_2CH_2$-	(16.5)
b, X = $CH_3CH_2CH_2O$-	(64)
c, X = $CH_3OCH_2CH_2$-	[-5][7]

The extrapolated viscosities of BCO 504 (14.4 cP at 20°C and 21.7 cP at 0°C) are higher than those for the dipentyl compound, but there appears to be a significantly different activation energy for the viscosities of the two systems such that the two-fold difference at 20°C has become very slight at 0°C.

1-n-Alkyl-4-n-alkoxybicyclo(2.2.2)octan-2-ones

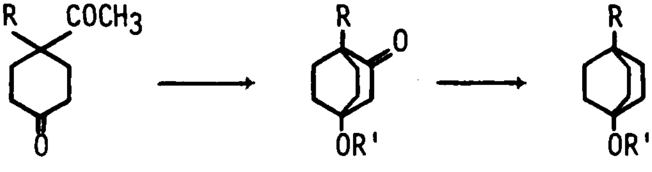
These compounds are precursors of the ethers mentioned above and their virtual T_{N-I} values are given in Table IV. Surprisingly, the T_{N-I} values of these compounds, although still very low, are higher than, or similar to the values for the alkyl-alkoxy compounds. Possibly the lateral carbonyl group, which for steric reasons would have been expected to reduce the lateral association of molecules, may have introduced stronger intermolecular dipolar associations, but since the virtual T_{N-I} values were obtained using a cyano host and since the extrapolations were long, it is conceivable that some interaction between the solute and the host may give a non-linear transition line.

What is according to expectation is that the broadening effect of the carbonyl group leads to a much higher viscosity than for dialkyl or alkyl-alkoxy compounds; for example, 4-butoxy-1-pentylbicyclo(2.2.2)octan-2-one has extrapolated viscosities of 55 cP at 20°C and 129 cP at 0°C.

EXPERIMENTAL

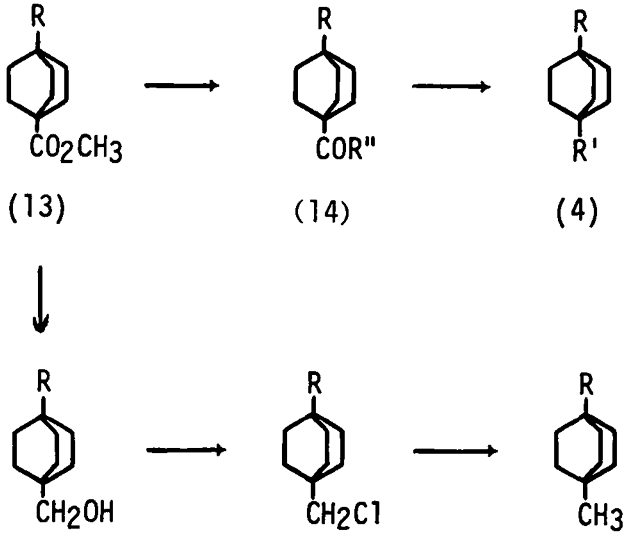
Materials

The diketones (12)[8] were treated with a trialkyl orthoformate in the corresponding alcohol as solvent and using toluene-*p*-sulphonic acid as catalyst to give (6);[9] subsequent Huang-Minlon reduction gave the 1-n-alkyl-4-n-alkoxybicyclo(2.2.2)octanes (5).



(12) (6) (5)

Methyl 4-n-alkylbicyclo(2.2.2)octane-1-carboxylates (13) were prepared by modifications to routes which have been reported previously.[10]



1-Methyl-4-pentylbicyclo(2.2.2)octane was prepared by lithium aluminum hydride reduction of ester (13), reaction of the primary alcohol with Ph_3P/CCl_4 and reduction of the chloromethyl compound with Li/t-BuOH/THF. 1-Pentylbicyclo(2.2.2)octane was produced by a similar reduction of 1-bromo-4-pentylbicyclo(2.2.2)octane, prepared from the methoxy-pentyl compound by reaction with acetyl bromide—stannic chloride.[11]

The ketones (14) were obtained from the esters (13) by reaction with a Grignard reagent in the presence of triethylamine.[12] The ketones were reduced by a Huang-Minlon procedure to give the 1,4-dialkylbicyclo(2.2.2)octanes (4).

Details of these experimental procedures are given in the thesis of H. M. Abdullah.[13] All materials prepared were checked for purity by the usual methods (t.l.c., g.l.c., h.p.l.c.) and the structures of all final products (and where necessary those of the synthetic intermediates) were confirmed by mass spectrometry, and n.m.r. and infrared spectroscopy.

Physical measurements

Transition temperatures were obtained by optical microscopy using a Nikon LKe polarising microscope equipped with a Mettler hot stage and control unit.

Viscosities were measured by standard procedures using capillary viscometers.

Acknowledgments

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