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Low-melting Bicyclo[2.2.2]octane Esters with Wide Range Nematic Phases

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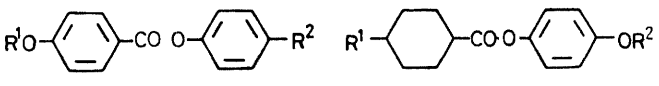
Summary A number of 4-alkylphenyl and 4-alkoxyphenyl-4-alkylbicyclo[2.2.2]octane-1-carboxylates have been prepared and several homologues have been found to exhibit wide-range nematic phases and to have melting points just above room-temperature.

Various esters derived from 4-alkylbicyclo[2.2.2]octan-1-carboxylic acids and different cyanophenols exhibit wide-range nematic phases of positive dielectric anisotropy.[1] Although these cyano-substituted esters were not particularly low-melting, their nematic phases persisted at higher temperatures than did those of analogous mesogens containing a 1,4-disubstituted benzene ring or a *trans*-1,4-disubstituted cyclohexane ring.

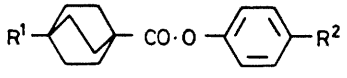
Esters with structures (**1**) and (**2**), where R^1, R^2 = n-alkyl, when mixed with other nematic materials of strong, positive dielectric anisotropy, may be used in electro-optical display devices with a multiplexed addressing system. The dialkyl systems corresponding to structures (**1**) and (**2**) also have interesting properties in this respect, but their nematic–isotropic (N-I) transition temperatures are rather low. We have now prepared the related 4-alkylphenyl and 4-alkoxyphenyl esters of 4-alkylbicyclo-[2.2.2]octane-1-carboxylic acid in order to obtain a new range of useful nematogens with higher N–I values than the corresponding esters with the ring systems shown in (**1**) and (**2**). The new materials also allow further comparisons between mesogens of structures which differ only in the presence of a benzene, a cyclohexane, or a bicyclo-octane ring.

The esters (**3**) were prepared from the known 4-alkylbicyclo[2.2.2]octane-1-carboxylic acids[1] and commercially available 4-alkyl- and 4-alkoxy-phenols according to a literature method.[1] Purification was achieved by column-chromatography and subsequent crystallisation or distillation. The structures of the esters (**3**) were established by



(**1**)

(**2**)



(**3**)

analyses of i.r., ^{1}H n.m.r., and mass spectra, and the purity of each ester was checked by t.l.c. and g.l.c.

These initial results show that a new family of nematogens with surprisingly low melting points, as well as high clearing points, has been produced. The N–I transition temperatures for both these new series of bicyclo[2.2.2]octane esters (**3**) are higher than those of the corresponding mesogens incorporating the 1,4-disubstituted benzene[2] or the *trans*-1,4-disubstituted cyclohexane[3] ring. For example, the esters corresponding to the 4/04 compound in the second part of the Table, but containing, instead of the bicyclo-

Table. Transition temperatures for the compounds (**3**).

R^1	R^2	Crystal–nematic (°C)	Nematic–isotropic (°C)
n-C_3H_7	n-C_5H_{11}	29·5	55·5
n-C_4H_9	n-C_5H_{11}	30	49
n-C_4H_9	n-C_7H_{15}	23	52
n-C_5H_{11}	n-C_5H_{11}	30	61
n-C_5H_{11}	n-C_6H_{13}	23·5	58·5
n-C_3H_7	n-OC_4H_9	40	92
n-C_4H_9	n-OC_4H_9[a]	32·5	84
n-C_5H_{11}	n-OC_4H_9	42	100
n-C_6H_{13}	n-OC_4H_9	48	93·5
n-C_5H_{11}	n-OC_6H_{13}	54·5	97

[a] Referred to as compound 4/04 in the text.

octane ring, a 1,4-disubstituted benzene ring and a *trans*-1,4-disubstituted cyclohexane ring, have respectively, the transition temperatures; crystal-nematic(C–N) 47 °C, N–I 45 °C and C–N 38 °C, N–I 68·5 °C. A similar comparison between the liquid crystal transition temperatures of the analogous dialkyl esters allows an identical order to be established. The order of decreasing N–I temperature is therefore confirmed for several distinct liquid crystal systems[1,4] as bicyclo-octane ring > cyclohexane ring > benzene ring.

Initial investigations of the physical properties of these esters at the Royal Signals and Radar Establishment show that the nematic phases of these esters are of low birefringence (Δn 0·075), dielectric anisotropy ($\Delta\epsilon$ − 0·61), and viscosity (η 110 cP at 0 °C; 34 cP at 20 °C; 12 cP at 50 °C). A more detailed report of the physical properties of the nematic phases of these esters will be made elsewhere,[5] but it seems that the low birefringence and dielectric anisotropy of these materials, in conjunction with certain other properties, will render them of use in some types of multiplexed twisted nematic displays.

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