172. Stable Liquid Crystals with Large Negative Dielectric Anisotropy. Part IV

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Summary

Stable liquid crystals with negative dielectric anisotropy containing the bicyclo[2.2.2]octyl group were synthesized. The incorporation of this moiety in the molecules increased the thermodynamic stability of the mesophase and lowered the smectic tendency. These new compounds can be useful in liquid crystal mixtures for homeotropic nematic displays.

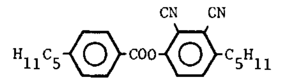
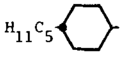
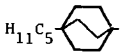
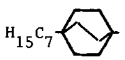
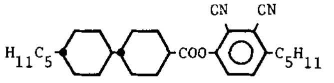
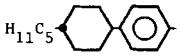
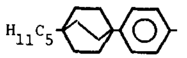
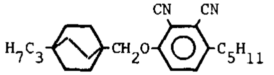
Introduction. – The need for stable nematogens with large negative dielectric anisotropy ($\Delta\varepsilon$) in 'guest-host' [1] [2] and homeotropic nematic (HN) [3] [4] displays was indicated earlier [5]. Compounds containing the 2,3-dicyanophenyl moiety were shown to possess the necessary large dipole moment across their long molecular axes and consequently large negative $\Delta\varepsilon$ [5] [6]. The benzoates as well as the cyclohexanoates of the 3-hydroxy-6-pentyl-1,2-benzenedicarbonitrile (**1**) were found to be more photochemically stable than the corresponding *p*-alkoxyphenyl esters owing to the absence of the quinonoid structure [6]. 4-*trans*-Substituted cyclohexanecarboxylates showed more tendency to give smectic phases than the corresponding benzoates [6].

Recently, it has been reported that an optimized HN-display requires a nematic mixture with relatively large $k_{33}/k_{11} = 2$ (k_{33}, k_{11} are the bend and splay elastic constants), and $\varepsilon_{\perp} \varepsilon_{\parallel} = 1.5$ ($\varepsilon_{\perp}, \varepsilon_{\parallel}$ are the dielectric constants perpendicular and parallel to the optical axis) [4]. An appreciable increase in k_{33}/k_{11} was obtained in the 4′-alkyl-4-cyanobiphenyls by replacing a phenyl group with a bicyclo[2.2.2]octyl moiety [7]. The same observation was made in the 4-alkylphenyl esters of 4-alkylbenzoic acids. Replacement of the cyclohexyl group in the phenyl esters of 4-*trans*-alkyl cyclohexanecarboxylic acids by a bicyclo[2.2.2]octyl moiety lead to the same result [8]. The phenyl esters of the 4-alkyl-bicyclo[2.2.2]octane-1-carboxylic acids have higher clearing points and lower tendency to give smectic phases than the corresponding esters of 4-*trans*-alkyl-cyclohexanecarboxylic acids [9]. These phenomena can be attributed to the influence of the bicyclo[2.2.2]octyl group on the 'lateral spacing' of the molecules and their packing [10].

We therefore studied the effect of replacing the benzoic acid and cyclohexanecarboxylic acid by a bicyclo[2.2.2]octane-1-carboxylic acid in the derivatives of dinitrile **1** on their mesomorphic properties.

Results and Discussion. – To obtain stable nematogens with large $\Delta\varepsilon$ and k_{33}/k_{11}, the 2,3-dicyano-4-pentylphenyl esters of 4-alkylbicyclo[2.2.2]octane-1-carboxylic acids and 4-(4-pentylbicyclo[2.2.2]octyl)benzoic acid were synthesized from the corresponding acid chlorides [9] [11] and phenol [6]. Their mesomorphic properties are compared to those of the corresponding benzoates and cyclohexanoates in the *Table.*

Table. *Effect of Replacing a Phenyl or a Cyclohexyl Group by a Bicyclo[2.2.2]octyl Moiety in 2,3-Dicyanophenyl Derivatives on their Mesomorphic Behaviour*[a])

		C		S		N		I	
2		.	59	–		–		.	[6]
3		.	70.0	.	(19.6)	–		.	[6]
4		.	84.0	–		–	(36.1)	.	
5		.	90.1	.	(37.3)	.	(48.7)	.	
6		.	87.7	.	154.2	.	168.6	.	[6]
7		.	106.1	–		.	(101.6)	.	[6]
8		.	130.9	–		.	137.9	.	
9		.	133.9	–		–		.	

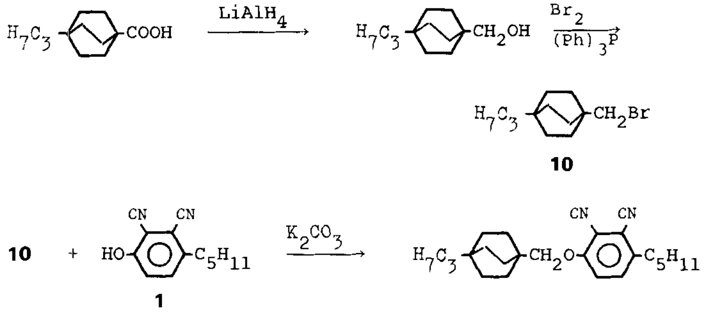
[a]) C = Crystalline, S = smectic, N = nematic, I = isotropic. Values given in brackets represent monotropic phases. A dot shows the existence of a phase transition while a dash indicates that the coresponding phase is missing. All values are given in °C.

Replacement of the phenyl group in the benzoate **2** by a *trans*-cyclohexyl moiety (compound **3**) led to a monotropic smectic phase with S-I transition at 19.6°. A bicyclo[2.2.2]octyl group instead of the cyclohexyl (compound **4**) gave rise to a monotropic nematic phase which cleared at 36.1°. No smectic phase could be observed, although the nematic phase was supercooled down to 20°. The bicyclo[2.2.2]octyl group not only suppressed the smectic tendency and favoured the nematic phase, but also enhanced the thermodynamic stability of the mesophase.

This is in accordance with the results of *Gray & Kelly* [9] in the corresponding laterally unsubstituted esters. Elongation of the alkyl chain (compound **5**) raised the clearing point and increased the smectic tendency, an observation which has been made in many other liquid crystalline series on going to the higher homologues [12]. A monotropic nematic phase with a relatively high clearing point is still observed on top of the smectic one.

An increase in the L/W-ratio (L = length and W = width of the rigid part of the molecule) usually leads to an increase in k_{33}/k_{11} [13], therefore the 4-(4-pentylbicyclo[2.2.2]octyl)benzoates are expected to have the desired elastic properties. The 2,3-dicyano-4-pentylphenyl ester (compound **8**) showed an enantiotropic nematic phase clearing at 137.9°. This is 36° higher than that of the corresponding cyclohexyl derivative **7**. The incorporation of a phenyl and a bicyclo[2.2.2]octyl group in the molecule enormously suppressed the smectic tendency and no smectic phase could be observed down to 35°, contrary to compound **6**.

Scheme



To lower the viscosity and enhance the thermal stability, the 4-propylbicyclo[2.2.2]oct-1-ylmethyl 2,3-dicyano-4-pentylphenyl ether was synthesized *(Scheme)*. However, its melting point was much higher than those of the esters and the melt could not be supercooled owing to its great tendency to crystallize.

Experimental Part

General. The mesomorphic properties were investigated by differential thermal analysis and polarizing microscopy using a *PE-DSC2* and a *Leitz Orthoplan* equipped with a modified *Mettler FP 5/52* heating stage. The hot-stage was cooled by means of a cold N_2 stream and the transition temperatures were measured at 0.2°/min heating rate. The differential thermal analysis was carried out at a rate of 5°/min. The GC purity of all products investigated was 99.7% or better as determined on a 1 m 3% *OV 25* open tubular column.

2,3-Dicyano-4-pentylphenyl 4-alkylbicyclo[2.2.2]octane-1-carboxylates **4** *and* **5**. A solution of the desired acid chloride (0.1M) [9], was added dropwise to a stirred solution of the dinitrile **1** (0.1M) [6] in pyridine and the mixture was heated at 80° for 1 h. The mixtures were worked up in the usual way and the products were crystallized from EtOH.

2,3-Dicyano-4-pentylphenyl 4-(4-pentylbicyclo[2.2.2]oct-1-yl)-benzoate (**8**) was prepared from the corresponding acid chloride [11] by the same method.

4-Propylbicyclo[2.2.2]oct-1-ylmethyl bromide (**10**). A solution of 0.14M 4-propylbicyclo[2.2.2]octane-1-carboxylic acid [9] in dry Et_2O was added dropwise to a stirred suspension of $LiAlH_4$ (0.3M) in dry Et_2O. The mixture was heated under reflux for 2 h, then worked up, and the resulting alcohol was obtained from the org. phase by distilling off the solvent. The IR spectrum of the product confirmed the presence of an alcoholic hydroxyl group.

Bromine (0.2M) was added during 5 min to a suspension of PPh_3 (0.2M) in CH_3CN at 0° and the mixture was stirred for 30 min at r.t. To this suspension, a solution of the previously prepared 4-propylbicyclo[2.2.2]oct-1-ylmethyl alcohol in acetonitrile was added dropwise and the mixture stirred for 15 min at r.t. The solvent was distilled off and the mixture heated at 130° for 30 min. After workup, the raw product was extracted in CH_2Cl_2 and purified by chromatography on silica gel in hexane to give a colourless liquid whose retention time on an *OV 25* column is longer than that of the alcohol.

2,3-Dicyano-4-pentylphenyl 4-propylbicyclo[2.2.2]oct-1-ylmethyl ether (**9**). K_2CO_3 (0.2M) was added to an equimolar mixture (0.1M) of **1** and **10** in dry $(CH_3)_2SO$. The stirred mixture was heated at 120° overnight, and then worked up. The product which was obtained by distilling off the solvent from the ethereal phase, was purified by chromatography (silica gel/toluene), then crystallized from EtOH. ^{1}H-NMR ($CDCl_3$): 0.90 (*m*, 6 H, 2CH_3); 1.2–2.0 (*m*, 22 H, 11 CH_2); 2.80 (*t*, 2 H, CH_2 next to arom. moiety); 3.70 (*s*, 2 H, CH_2O); 7.1 (*d*, $J = 9$, 1 H, arom. H); 7.4 (*d*, $J = 9$, 1 H, arom. H).

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