180. Some Novel Nematic Materials Bearing Two Lateral Nitrile Functions

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Summary

More than fifty esters of 3-alkyl-6-hydroxy-1,2-benzenedicarbonitrile have been prepared. The new esters exhibit stable nematic phases of high negative dielectric anisotropy. The relationship between the clearing points of the esters and the various rings they incorporate is the same as that normally observed for nematic materials of positive dielectric anisotropy.

Introduction. – Most commercially available electro-optic displays utilising liquid crystals are based on the twisted nematic mode of operation [1]. These devices contain nematic mixtures of high positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_1 - \varepsilon_2 \cong +10$). However, this type of display does not meet all the requirements of certain applications.

Other types of liquid crystal displays, such as the 'guest-host' *Heilmeier* and cholesteric-nematic phase-change devices [2], and displays based on the deformation of a homeotropically aligned nematic layer [3], are receiving considerable attention as possible alternatives to the twisted nematic displays. However, the guest-host displays with positive contrast [2] and the displays based on electrically controlled birefringence require nematic mixtures of negative dielectric anisotropy (*e.g.* $\Delta\varepsilon \cong -5$) [2] [3]. At present the only commercially available nematic mixtures of high negative dielectric anisotropy are those (*eg. EN18* and *EN24*) offered by the *Chisso Corporation* [4]. These mixtures contain dicyano-hydroquinone derivatives (*e.g.* aromatic esters of 3-alkoxy-6-hydroxy-1,2-benzenedicarbonitrile). It is the resultant dipole moment due to the two lateral nitrile groups perpendicular to the long axis of these hydroquinone derivatives that gives rise to the large negative value of the dielectric anisotropy of the nematic mixtures (*e.g. EN18:* $\Delta\varepsilon \cong -6$ at 25°) containing them. However, the 3,6-dihydroxy-1,2-benzenedicarbonitrile moiety is a good leaving group in substitution and eliminations. As a consequence the thermal and photochemical stability of nematic mixtures containing them are insufficient for fully satisfactory use in display devices.

Replacement of the alkoxy-substituent of this dinitrile by an alkyl group should result in a lower leaving-group efficiency for the resultant 3-alkyl-6-hydroxy-1,2-

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benzenedicarbonitrile, which still retains the large, *trans*-axial, resultant dipole moment. Thus, esters of this dinitrile should exhibit a greater degree of thermal and photochemical stability than the analogous esters containing the alkoxy-substituted dinitrile. If this were actually found to be so, then these esters would be of commercial interest for display devices requiring mixtures of negative dielectric anisotropy. Therefore we synthesized 3-hydroxy-6-pentyl-1,2-benzenedicarbonitrile [5], and 3-heptyl-6-hydroxy-1,2-benzenedicarbonitrile to prepare appropriate esters.

It was decided to substitute the novel 3-alkyl-6-hydroxy-1,2-benzenedicarbonitriles for the 4-alkylphenols of the known esters [8–10] which possess high nematic-isotropic liquid transition temperatures. Incorporation of lateral substituents into liquid crystal molecules generally results in a decrease (often substantial) of the clearing points [6]. Moreover introduction of a nitrile function into a number of compounds exhibiting nematic phases has resulted in large decreases in the nematic-isotropic liquid transition temperature [7]. However, it was expected that by preparing esters of 3-alkyl-6-hydroxy-1,2-benzenedicarbonitrile, whose unsubstituted analogues [8–10] (with H-atoms in place of the CN-groups) exhibit very high nematic-isotropic liquid transition temperatures, the new dicyano-substituted esters would possess at least moderately high clearing points, despite the presence of the nitrile functions.

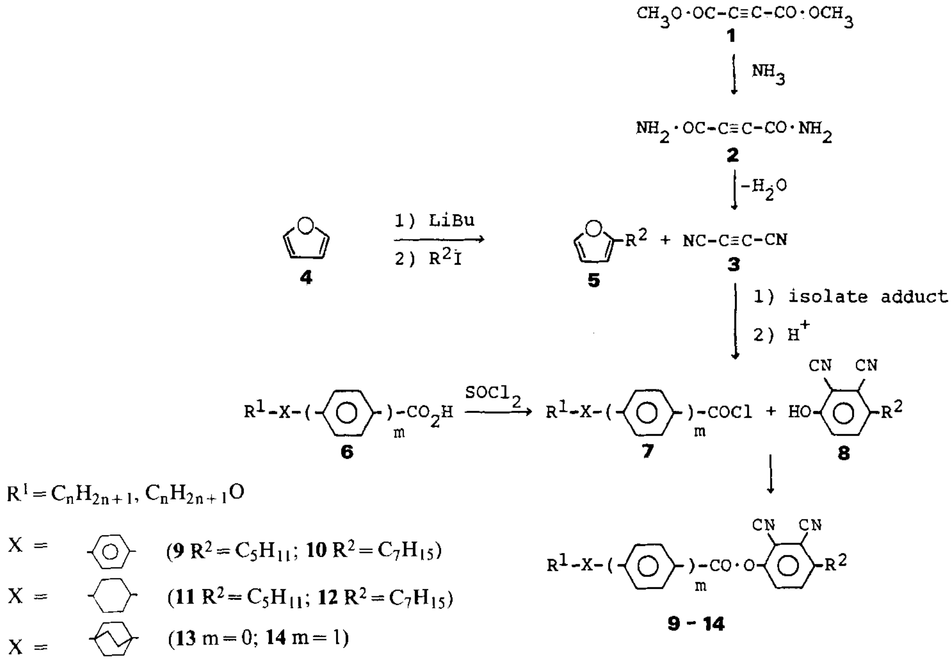
The acid parts of the esters were constituted from those ring-systems most commonly found in thermotropic compounds exhibiting liquid crystal properties, *i.e.* 1,4-disubstituted benzene, cyclohexane and bicyclo[2.2.2]octane. This presented the first opportunity to study a variety of homologous series of nematic liquid crystals containing these ring-systems and a large resultant dipole moment *perpendicular* to the long axis of the molecule.

Results and Discussion. – The 4-alkylbicyclo[2.2.2]octane-1-carboxylic acids (**6**, m = 0; see the *Scheme*) were prepared according to [11]. The other acids required (**6**, m = 1; X = 1,4-disubstituted benzene [12], *trans*-1,4-disubstituted cyclohexane [13], or 1,4-disubstituted bicyclo[2.2.2]octane [14] see the *Scheme*) were prepared by hydrolysis of the corresponding nitriles (see *Exper. Part*). These were either commercially available or could be synthesized [14]. The acids **6** were readily converted to the corresponding acid chlorides **7**. The 3-alkyl-6-hydroxy-1,2-benzenedicarbonitriles (**8**; $R^2 = C_5H_{11}$ and $R^2 = C_7H_{15}$) were prepared *via* hydrolysis in acidic medium of the *Diels-Alder* adduct [5] of acetylenedinitrile (**3**) [15] and 2-alkylfuran (**5**). The esters **9–14** were prepared *via* the reaction of the relevant acid chlorides **7** and dinitriles **8** in the presence of pyridine [11] (see the *Scheme*).

The liquid crystal transition temperatures (C–N/I, N–I) and several enthalpies of fusion (ΔH) of the 2,3-dicyano-4-pentylphenyl, and 2,3-dicyano-4-heptylphenyl 4′-alkyl(or alkoxy)-4-biphenyl-1-carboxylates (**9** and **10**, respectively; m = 1; X = benzene [16]) are listed in *Table 1* and *Table 2*. The liquid crystal transition temperatures of the pentylphenyl esters **9** (R^1 = alkyl and R^1 = alkoxy) are plotted against the number of the C-atoms (n) in the terminal C-chain attached to the acid part of the esters in *Fig. 1* and *2*.

It can be seen from *Table 1* and *Fig. 1* that except for the value for the first member of the series (n = 1) the clearing points (N–I) of the alkyl esters rise

Scheme



gradually as the alkyl chains lengthen. As usual, the plot of the clearing points of the esters having an even number of C-atoms (n=2, 4, 6, 8) lies below that of the esters with an odd number in the alkyl chain (n=1, 3, 7). Thus the normal pattern of alternation is observed. The melting points are irregular, but show a general

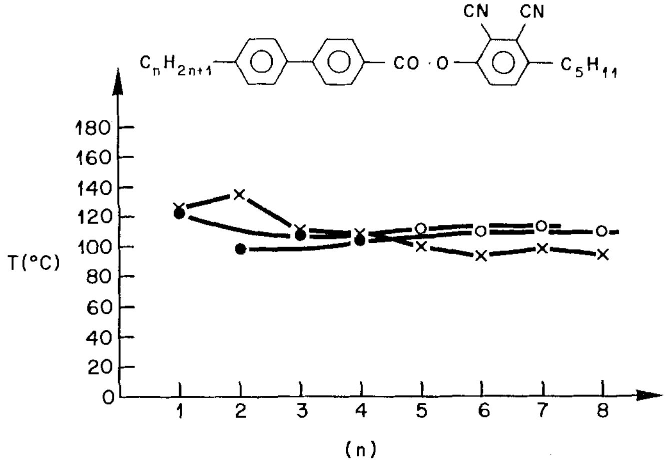


Fig. 1. *Plot of the transition temperatures* vs. *the number of* CH_2*-groups* (n) *in the C-chain* (C_nH_{2n+1}) *of the esters formulated* (X, crystal-nematic transition; ○, enantiotropic nematic-isotropic liquid transition; ●, monotropic nematic-isotropic liquid transition)

tendency to decrease with increasing alkyl chain length. The early members of the series (n = 1–4) exhibit monotropic nematic phases, while all the other homologues possess enantiotropic nematic phases. The plots of the liquid crystal transition temperatures of the alkoxy esters against the number of methylene units (n) in the terminal alkoxy-chain are very similar *(Fig. 2)*. The clearing points (N–I) decrease with increasing alkyl chain length (n → 1–7) and do not rise at all, at least for the alkoxy chain lengths studied. The replacement by an O-atom of the CH_2-group adjacent to the benzene ring of the acid moiety of the alkyl esters **9** to produce the alkoxy-esters increases the clearing points (+*ca.* 50°, on average) more than the melting points (+25°, on average). All of the nematic phases of the alkoxy-substituted esters **9** are enantiotropic.

The liquid crystal transition temperatures and some enthalpies of fusion of the 2,3-dicyano-4-heptylphenyl 4′-alkyl (or alkoxy)-4-biphenyl-1-carboxylates **10** (m = 1; X = benzene) are listed in *Table 2*. The liquid crystal transition temperatures of the alkyl/alkoxy heptylphenyl esters **10** are similar to those of the corresponding pentylphenyl esters **9**. However, in almost every case, the alkyl/alkoxy heptylphenyl esters exhibit lower melting points (–14° and –0.5°, on average, respectively), and lower clearing points (–2.5° and –6°, on average), than the analogous pentylphenyl esters. The nematic ranges of the heptylphenyl alkyl-esters **10** are therefore somewhat wider (*ca.* +11.5°, on average) then those of the corresponding pentylphenyl alkyl-esters **9**. The nematic ranges of the heptylphenyl alkoxy-esters **10** are a little narrower (*ca.* –5.5°, on average) than those of the analogous pentylphenyl alkoxy-esters **9**. These results are in accord with the behaviour observed for materials of strong positive dielectric anisotropy and weakly positive or negative dielectric anisotropy, *i.e.* alkoxy derivatives exhibit higher nematic-isotropic transition temperatures than the corresponding alkyl derivatives (when attached to aromatic rings).

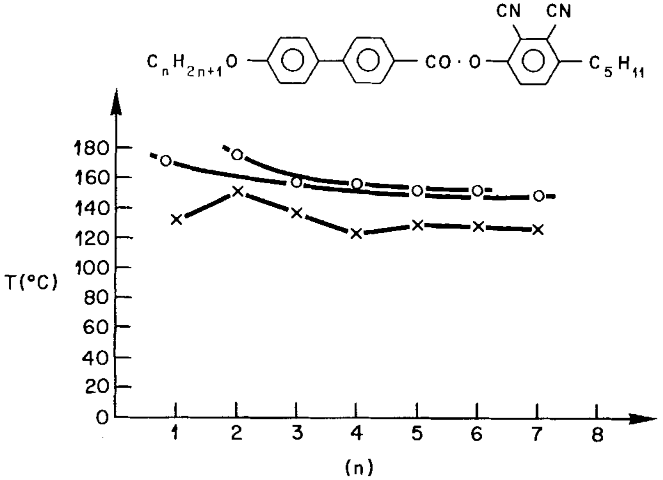


Fig. 2. *Plot of the transition temperatures* vs. *the number of CH_2-groups* (n) *in the C-chain* (C_nH_{2n+1}) *of the esters formulated* (X, crystal-nematic transition; ○, enantiotropic nematic-isotropic liquid transition)

All the measured enthalpies of fusion (*Δ H*) of the esters **9** and **10** are of the usual order of magnitude for thermotropic liquid crystals.

The liquid crystal transition temperatures of six esters ($m=1$; $X=$ *trans*-1,4-disubstituted cyclohexane; **11**, $R^2=C_5H_{11}$; **12**, $R^2=C_7H_{15}$) are recorded in *Table 3*. The pentylphenyl esters **11** containing the *trans*-1,4-disubstituted cyclohexane ring, exhibit higher melting points (*ca.* +9°, on average) and lower clearing points (*ca.* –13.5°, on average) than the corresponding esters **9**, incorporating a benzene ring in place of the cyclohexane ring. A similar situation is observed for the heptylphenyl esters **12**, when compared with the corresponding fully aromatic esters **10**, however the difference in melting points (*ca.* +28°, on average) and clearing points

Table 1. *Transition Temperatures (°C) and Enthalpies of Fusion (*Kcal · mol^{-1}*) for Compounds* **9**

R	C-N/I	N-I[a])	ΔH
CH_3	125	(122)	
C_2H_5	135	(98.5)	
C_3H_7	109.5	(108)	7.6
C_4H_9	108.5	(103)	8.4
C_5H_{11}	99	112.5	7.3
C_6H_{13}	93	109	7.6
C_7H_{15}	98	113	7.5
C_8H_{17}	94.5	109.5	8.0
CH_3O	133.5	168	
C_2H_5O	151	174	
C_3H_7O	137	157	
C_4H_9O	123	156	
$C_5H_{11}O$	129.5	151.5	
$C_6H_{13}O$	128.5	152	5.8
$C_7H_{15}O$	125.5	149	

[a]) () Represents a monotropic transition temperature.

Table 2. *Transition Temperatures (°C) and Enthalpies of Fusion (*Kcal · mol^{-1}*) for Compounds* **10**

R	C-N/I	N-I[a])	ΔH
CH_3	118.5	(115)	
C_2H_5	102	(94.5)	
C_3H_7	95.5	103.5	
C_4H_9	87.5	100	7.0
C_5H_{11}	93	110	7.6
C_6H_{13}	83.5	108	2.8
C_7H_{15}	86.5	112	
C_8H_{17}	84	110.5	2.7
CH_3O	126	158	
C_2H_5O	149.5	164.5	
C_3H_7O	133	150	
C_4H_9O	124.5	153	
$C_5H_{11}O$	132	147	
$C_6H_{13}O$	131	148	
$C_7H_{15}O$	127.5	146.5	

[a]) () Represents a monotropic transition temperature.

(*ca.* – 15°, on average) are even greater. For the esters **9** the replacement of the terminal pentyl chain on the phenolic moiety with a heptyl chain to produce the esters **10** resulted in an increase in nematic range (*ca.* + 11.5°); for the cyclohexane ester derivatives **11** and **12** the reverse occurs and the nematic-isotropic liquid transition temperature becomes even more strongly monotropic (*i.e.* approximately 13° further beneath the melting point). It is interesting to note that the nematic-isotropic liquid transition temperatures of the esters **11** and **12** containing a *trans*-1,4-disubstituted cyclohexane are generally lower (*ca.* – 15°, on average) than those of the corresponding esters **9** and **10** containing a 1,4-disubstituted benzene in place of the cyclohexane. This phenomenon has also been observed for three-ring systems incorporating a terminal CN-function parallel to the long molecular axis [18]. For two-ring systems this is seldom the case [18].

The replacement of the benzene ring in the acid part of the esters **12** (*e.g.* $R^1 = C_5H_{11}$; $R^2 = C_7H_{15}$) by a *trans*-1,4-disubstituted cyclohexane to produce a dicyclohexyl ester causes a large increase in the clearing point (*i.e.* N – I = 164°, *cf.* *Table 3*). A smectic-nematic transition (S_A – N = 160.5°) is also observed, and the

Table 3. *Transition Temperatures (°C) and Enthalpies of Fusion (*Kcal · mol⁻¹*) for Compounds* **11** *and* **12**

R_1	R_2	C-I	N-I	ΔH
C_3H_7	C_5H_{11}	118	(89)	7.7
C_5H_{11}	C_5H_{11}	106	$(102)^{5,17}$	7.5
C_7H_{15}	C_5H_{11}	109	(103)	8.2
C_3H_7	C_7H_{15}	131	(84)	
C_5H_{11}	C_7H_{15}	116.5	(98.5)	
C_7H_{15}	C_7H_{15}	114	(99.5)	

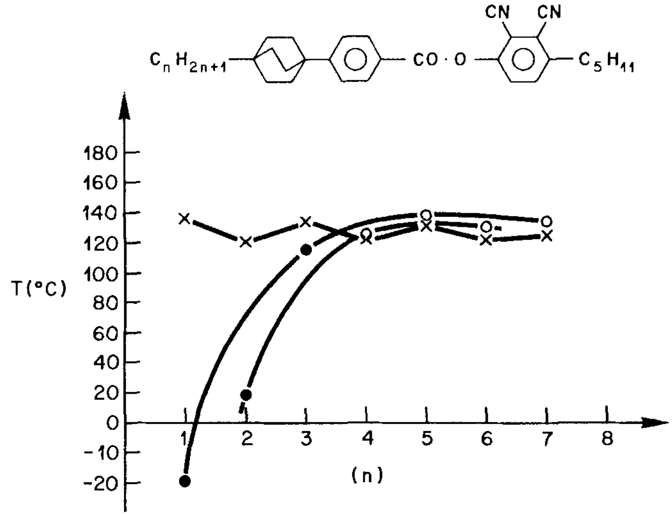


Fig. 3. *Plot of the transition temperatures* vs. *the number of* CH_2*-groups* (n) *in the C-chain* (C_nH_{2n+1}) *of the esters formulated* (X, crystal-nematic transition; ○, enantiotropic nematic-isotropic liquid transition; ●, monotropic nematic-isotropic liquid transition)

melting point is considerably decreased ($C-S_A=87°$). The nematic range of this new ester, *i.e.* 4-heptyl-2,3-dicyanophenyl all-*trans*-4-(4-pentylcyclohexyl)cyclohexane-1-carboxylate is therefore narrow (3.5°).

The clearing points of the *trans*-4-(4-alkylcyclohexyl)-benzoates **11** and **12** are lowest for the propyl homologues, and are almost equal for the pentyl and heptyl homologues. The melting points of both series are highest for the propyl homologue and approximately the same for pentyl and heptyl. Thus, on ascending the series, the nematic phases of the esters **11** and **12** become less strongly monotropic.

Two series of esters **13** and **14** were produced by reation 3-hydroxy-6-pentyl-1,2-benzenedicarbonitrile with five 4-alkylbicyclo[2.2.2]octane-1-carboxylic acids [11] and seven 4-(4-alkylbicyclo[2.2.2]oct-1-yl)benzoic acids [14]. The liquid crystal transition temperatures of the esters [19] are recorded in *Table 4* and plotted (for esters **14**) against the number of C-atoms (n) in the terminal alkyl chain of the acid moiety in *Fig. 3*. Enthalpies of fusion for several of the esters are also listed in *Table 4*. They are of a similar magnitude to those in *Tables 1–3*.

While the melting points of the bicyclo-octane esters do not show any significant trends, the clearing points of both series rise from very low values (> 20°) for short alkyl chains (**13**, $n<4$; **14**, $n=1$ and 2) to high values for longer alkyl-chains *(Table 4)*. The normal pattern of alternation is again observed. The melting points of both the esters **13** ($C-I \cong 82.5°$, on average) and the esters **14** ($C-N/I \cong 127°$, on average) are high. Indeed, all the nematic phases of the bicyclo-octane esters **13** are strongly monotropic.

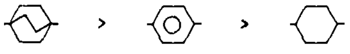
The clearing point ($N-I=(36°)$) of the dipentyl-substituted dicyano-ester **13** is higher than that ($N-I=(29.5°)$) of the corresponding monocyano-ester, with the CN-function in the 2-position [7]. Such behaviour has already been observed for the analogous esters incorporating a *trans*-1,4-disubstituted cyclohexane in place of the bicyclo-octane [5]. The presence of smectic phases for the homologues with longer alkyl chains (**13**, $R=C_6H_{13}-C_8H_{17}$) is noteworthy. Neither the corresponding esters where the CN-groups are replaced by H-atoms [11], nor the corresponding dicyano-substituted bicyclooctane esters **14** exhibit smectic phases (despite substantial super-cooling below the melting point down to room temperature for the esters **14**).

Table 4. *Transition Temperatures (°C) and Enthalpies of Fusion (*Kcal · mol^{-1}*) for Compounds* **13** *and* **14**

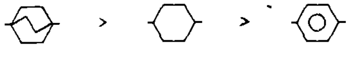
R	m	C-N/I	S_A-N[a])	N-I[a])	*ΔH*
C_4H_9	0	73		(17)	5.8
C_5H_{11}	0	84		(36)^{19}	
C_6H_{13}	0	81.5	(30)	(39)	6.5
C_7H_{15}	0	90	(37)	(49)^{19}	
C_8H_{17}	0	84	(44)	(51)	7.4
CH_3	1	136		(– 20°C)	
C_2H_5	1	120		(18.5)	
C_3H_7	1	134		(115)	
C_4H_9	1	123		125	5.1
C_5H_{11}	1	131		138^{19}	7.4
C_6H_{13}	1	122		130	6.0
C_7H_{15}	1	125		134	7.25

[a]) () Represents a monotropic transition temperature.

While the average melting point (*ca.* 127°) of the esters **14** is higher than that of the corresponding cyclohexane esters **11** (*ca.* 111°) and fully aromatic esters **9** (*ca.* 108°), the average clearing point (*ca.* 93°) is lower than those (*ca.* 108° and 98°) of the esters **9** and **11**. However, when the values for the first two members of the series are neglected then the average clearing point (*ca.* 128°) of the bicyclooctane esters **14** is higher than either that of the corresponding cyclohexane esters (*ca.* plus 30°) or that of the analogous phenyl esters (*ca.* plus 20°). Indeed, this behaviour has been observed for similar systems incorporating a strong dipole moment (in the form of a terminal CN-function) parallel to the long molecular axis of other nematic systems [18]. Thus for the esters **9**, **11** and **14**, which differ only by one of the ring systems under study, the order of decreasing clearing point (for the higher homologues) appears to be:



From the small number of clearing points available for esters of 3-hydroxy-6-pentyl-1,2-benzenedicarbonitrile with two-ring systems (*i.e.* comparing the dipentyl homologues of the bicyclooctane-esters **13** (N – I = 36°), the corresponding cyclohexane ester (N – I = 20°) [5] and the analogous benzoate (N – I > 20°) [5]) the order of decreasing point appears to be:



This is the order of decreasing nematic-isotropic liquid transition temperature which is normally observed for similar nematic systems containing a terminal CN-function [6].

The nematic-isotropic liquid transition temperatures of the esters **9**, **11** and **14** are lower (*ca.* 60–70°) than those of the corresponding esters [8–10] where the CN-functions have been replaced by H-atoms. However, while the latter esters [8–10] exhibit high smectic-nematic transition temperatures (S – N ≅ 130–170°), *no* smectic phases could be observed for the analogous dicyano-substituted esters **9**, **11** and **14**. Thus, as is often the case, the introduction of lateral substituents into liquid crystal molecules results in a much stronger depression of the smectic-nematic transition temperatures than the nematic-isotropic transition temperatures. However, the dangers of generalising are demonstrated by the presence of smectic phases in the bicyclooctane-esters **13**. No discernable 'shielding effect' by the aliphatic rings [7] is exhibited by the esters **9–14**.

Physical Properties. – The dielectric anisotropy of the esters **9–14** is large and negative, *e.g.* for the fully aromatic ester **9** ($R^1 = C_5H_{11}$) $\Delta\varepsilon = -11.7$ at 0.95 T_{N-I} [20]. The thermal and photochemical stability of several homologues of the esters **9–14** in admixture with 4-alkoxyphenyl *trans*-4-alkylcyclohexane-1-carboxylates has been determined. The life-times of these mixtures, when subjected to thermal and UV tests, are significantly greater than those of the *Chisso* mixtures *EN18* and *EN24*, under identical conditions. As can be seen from *Tables 1–4*, the enthalpies of fusion of the esters **9–14** are of a magnitude to allow them to be used as components in low-melting nematic mixtures. A far more extensive report of the physical properties of the esters **9–14** is under preparation [20].

Experimental Part

(Mr. *F. Rime* is thanked for excellent technical assistance)

General. The liquid crystal transition temperatures of the compounds **9**–**14**, recorded in *Tables 1–4*, were determined by optical microscopy using a *Leitz Orthoplan* microscope in conjunction with a *Mettler FP52* heating stage and *FP5* control unit. All the monotropic liquid crystal phases could be observed using a microscope and no virtual values (extrapolated) had to be determined. When necessary, the *Mettler* stage could be cooled ($< -20°$) by allowing N_2 gas, cooled by liquid N_2, to pass through the stage at a controlled rate. The enthalpies of fusion of the highest melting crystalline phases of the esters (**9**–**14**) were determined using a *Perkin Elmer DSC-2* differential scanning calorimeter equipped with a *Hewlett Packard 3380A* integrator. Indium was used as a standard for calibration.

The purity of the compounds was determined by thin layer chromatography (TLC) and gas chromatography (GC). A *Perkin Elmer Sigma 1* gas-chromatographic system and also a *Perkin Elmer 3920B* gas chromatograph with a *Hewlett Packard 3380A* integrator were used. The structures of the compounds were confirmed, by analysis of their IR, ^{1}H-NMR and mass-spectra. The instruments used were a *Brucker WP 200* NMR spectrometer, a *Perkin Elmer PE683* IR spectrophotometer with model *3600* data station, and a *Hitachi RMU 6L* mass spectrometer. Combustion analysis was also carried out.

2-Pentylfuran (**5**, $R^2 = C_5H_{11}$). A solution of BuLi (251 g, 0.587 mol) in hexan was added dropwise over 40 min to a solution of 60 g (0.881 mol) of furan in 400 ml of dry THF at −25° under anh. conditions. After the addition, the solution was stirred at −15° for a further 6 h. The solution was cooled again to −25° and 93 g (0.47 mol) of freshly destilled pentyl iodide was added dropwise over 20 min. After the addition, the temperature of the resultant solution was gradually allowed to re-attain r.t. and then stirred overnight. Brine was added and the org. layer separated. The aq. layer was extracted with Et_2O and the combined org. layers washed with brine and dried ($MgSO_4$). A little antioxidant was added to the filtered solution, which was evaporated under slightly reduced pressure, and the residue distilled under reduced pressure (bp. 78–79°/58 Torr) to yield pure product (75.5 g, 62%). IR (Film): 2900 (CH_2), 1600, 1510, 1450 (C=C). MS: 138 (M^+).

$C_9H_{14}O$ (138.21) Calc. C 78.26 H 10.15% Found C 78.44 H 10.38%

2-Heptylfuran (**5**, $R^2 = C_7H_{15}$) was prepared similarly (65%), bp. 110–111°/44 Torr). IR (Film): 2900 (CH_2), 1600, 1510, 1450 (C=C). MS: 166 (M^+).

$C_{11}H_{18}O$ (166.27) Calc. C 79.46 H 10.9% Found C 78.83 H 11.5%

3-Hydroxy-6-pentyl-1,2-benzenedicarbonitrile (**8**, $R^2 = C_5H_{11}$). A solution of 16 g (0.115 mol) of freshly destilled 2-pentylfuran and 30 ml of dry THF was added dropwise over 20 min to a solution of 9.65 g (0.127 mol) of freshly destilled acetylenedinitrile in 30 ml of dry THF at 0° maintained under anh. conditions. The resultant solution was stirred at 0° overnight and allowed gradually to re-attain r.t. The solvent was removed under vacuum and the residue taken up in a minimum of solvent and eluted from a silica-gel column using $CHCl_3$. Fractions containing product were evaporated together and the residue (24 g) was taken up in 350 ml of CH_2Cl_2. The resultant solution was cooled to 0° and 25 ml of conc. H_2SO_4 was added dropwise, whilst maintaining the temperature at 0°. The resultant mixture was allowed to reach r.t. and stirred for a further 4 h. The mixture was then poured into ice and the org. phase separated. The aq. phase was extracted with Et_2O and the combined org. layers were evaporated. The residue was taken up in Et_2O and the resultant solution extracted with 1N NaOH. The combined aq. extracts were washed twice with Et_2O and then acidified with cold, dil. HCl. The liberated phenol was extracted into Et_2O and the combined org. extracts washed with brine and dried ($MgSO_4$). The solvent was removed under vacuum and the residue was taken up in a small volume of solvent and eluted from a silica-gel column with toluene/AcOEt 2:1. Single-spot fractions containing phenol were combined and evaporated under vacuum. The resultant residue was boiled with active charcoal in AcOEt and then crystallized from toluene. The yield of pure (99.9%) phenol was 15 g (60.5%) mp. 142°, dec. IR (KBr): 3230 (OH), 2225, 2215 (CN), 1310 (C–O), 850 (phenyl). MS: 214 (M^+).

$C_{13}H_{14}N_2O$ (214.27) Calc. C 72.87 H 6.58% Found C 73.14 H 6.38%

3-Heptyl-6-hydroxy-1,2-benzenedicarbonitrile (**8**, $R^2 = C_7H_{15}$) was prepared as above (yield 64%; m.p. 115°, 99.9% pure). IR (KBr): 3230 (OH), 2225, 2215 (CN), 1310 (C–O), 850 (phenyl). MS: 242 (M^+).

$C_{15}H_{18}N_2O$ (242.32) Calc. C 73.34 H 7.49% Found C 69.71 H 7.76%

4'-Pentylbiphenyl-4-carboxylic acid (**6**, *m* = *1*, $R^1 = C_5H_{11}$, *X* = *Ph*). A mixture of 10 g (0.04 mol) of 4'-pentyl-4-cyanobiphenyl, 100 ml of 50% (v/v) H_2SO_4, and 200 ml of glacial AcOH were heated at 120° overnight. The precipitated product, filtered off from the reaction solution upon cooling to r.t., was washed with small volumes of H_2O, pressed dry, and then crystallized from EtOH to yield pure product (9.5 g, 88%; C–S = 177°; S–N = 243°; N–1 = 269°; [12] C–S = 176°; S–N = 243°;N–I = 268°). IR (KBr): 3000 (OH), 1690 (C=O), 1610, 1520, 1420 (phenyl). MS: 252 (M^+).

4'-Pentylbiphenyl-4-carbonyl chloride (**7**; $R^1 = C_5H_{11}$, *m* = *1*, *X* = *Ph*). A solution of 1 g (0.0037 mol) of **6** ($R^1 = C_5H_{11}$) and 25 ml of $SOCl_2$ was heated at 80° for *ca.* 1 h under anh. conditions. The excess of $SOCl_2$ was removed under vacuum and 10 ml of Na-dried toluene was added to the residue and then removed under vacuum. A further ml of Na-dried toluene was added and the process repeated. The residue of acid chloride was used in the next reaction without further purification.

2,3-Dicyano-4-pentylphenyl 4'-pentylbiphenyl-4-carboxylate (**9**, $R^1 = C_5H_{11}$, *m* = *1*, *X* = *Ph*). A solution of 0.8 g (0.0037 mol) of **8** ($R^2 = C_5H_{11}$) in 5 ml sieve-dried pyridine was added to a solution of **7** ($R^1 = C_5H_{11}$, m = 1, X = Ph) (0.0037 mol) in 10 ml of Na-dried toluene maintained under anh. conditions. The resultant solution was the heated under gentle reflux for 1 h. The cooled reaction mixture was added to cold, dil. HCl and extracted with $CHCl_3$. The combined org. layers were washed with H_2O and dried ($MgSO_4$). The filtered solution was evaporated and the residue taken up in a minimum of solvent and eluted from a silica-gel column with toluene. Single-spot fractions containing the ester were combined and evaporated together to yield the desired product, which was crystallized from EtOH until constant transition temperatures were observed (see *Tables 1–4* for the liquid crystal transition temperatures of this ester and the esters **9–14** prepared by the procedure. The yields of crude product were quantitative). IR (KBr): 2215 (CN), 1695 (C=O). MS: 464 (M^+); 251 ($C_{18}H_{19}O^+$).

$C_{31}H_{32}N_2O_2$ (454.61) Calc. C 80.14 H 6.94 N 6.03% Found C 80.05 H 6.80 N 6.07%

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