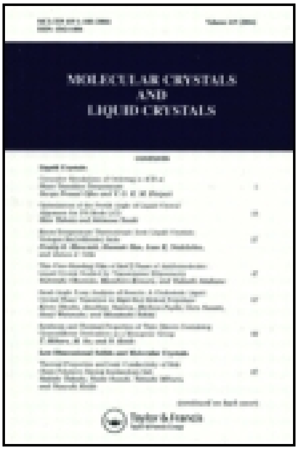

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Some Novel Nematic Liquid Crystals of Negative Dielectric Anisotropy

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To cite this article: S. M. Kelly & Hp. Schad (1984): Some Novel Nematic Liquid Crystals of Negative Dielectric Anisotropy, Molecular Crystals and Liquid Crystals, 110:1-4, 239-261

To link to this article: http://dx.doi.org/10.1080/00268948408074508

Mol. Cryst. Liq. Cryst. 1984, Vol. 110, pp. 239-261
0026-8941/84/1104-0239/$18.50/0

SOME NOVEL NEMATIC LIQUID CRYSTALS OF NEGATIVE DIELECTRIC ANISOTROPY

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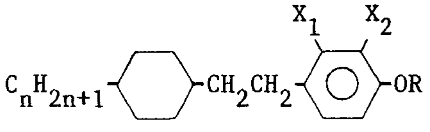
A number of ether and ester derivatives of 1-(trans-4-n-alkylcyclohexyl)-2-(4-hydroxyphenyl)ethane bearing lateral substituents on the phenyl ring are reported. Several of the novel compounds exhibit enantiotropic nematic phases at room temperature. All of the liquid crystals described are of negative dielectric anisotropy (-0.5 → -3.5). The effect of lateral substituents on the liquid crystal transition temperatures of these ethanes has been studied.

1. INTRODUCTION

The ethyl linkage between aromatic and/or aliphatic rings has been studied recently as a possible alternative to the ester linkage in nematic liquid crystals used in display devices.[1-8] Liquid crystals incorporating the ethyl linkage ($-CH_2CH_2-$) generally possess the advantages, when compared to the analogous compounds containing the ester linkage (-CO·O-), both of lower viscosity and lower melting point.[1-7] A disadvantage of the ethanes is that the large majority of those synthesized exhibit high smectic-nematic/isotropic transition temperatures (S-N/I).[1-3,5-7] This limits the concentration of these compounds in nematic mixtures for display applications. A possible way of producing ethyl compounds, with properties nearly identical, to those of the known ethanes[1-7] but with much lower smectic-nematic/isotropic transition temperatures, is to introduce small lateral substituents on the phenyl ring.[9-13] The laterally substituted ethanes are expected to possess marginally lower nematic-isotropic transition temperatures (N-I) and somewhat higher viscosities.[9-13]

In order to investigate the effect of lateral substitution on the liquid crystal transition temperatures of compounds containing an ethyl central linkage, we have synthesized the following substituted ethanes (I):



(I)

where one of the lateral substituents (X_1 or X_2) is a hydrogen atom and the other one is either a halogen atom (F, Cl, or Br) or a nitrile function (CN); R may be a normal alkyl chain, a *trans*-4-n-alkylcyclohexylmethyl- or a *trans*-4-n-alkylcyclohexyl-1-carboxy-group (i.e. -OR, represents an ether or an ester function).

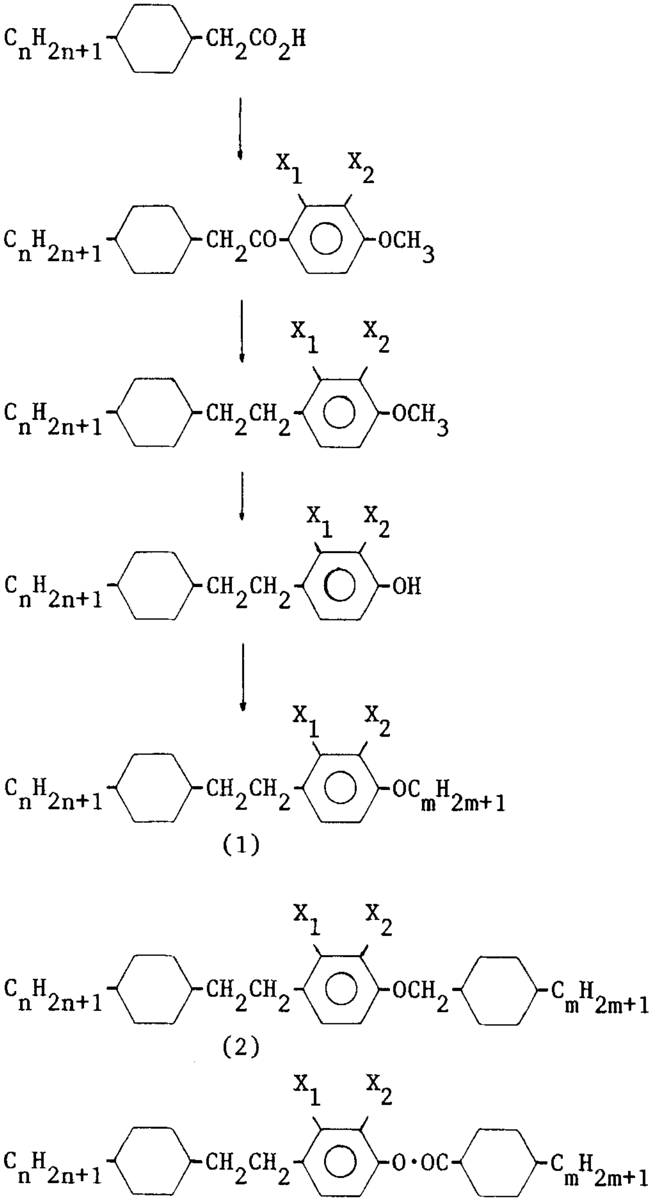
The large majority of the novel ethanes (I) which we have synthesized incorporate a lateral fluoro-substituent (X_1 or X_2 = F), as they are the ones most likely to be useful as additives of low viscosity for commercial nematic mixtures.[9-13] Two three-ring ethanes (I) containing either a chlorine or a bromine atom (X_2 = Cl or Br) were synthesized in order to establish a quantitative relationship between the liquid crystal transition temperatures and the size of the lateral substituent.

The nematic phases of ethanes (I) incorporating polar substituents in a lateral position would be expected to be of moderately strong negative dielectric anisotropy. Compounds of moderate-to-strong negative dielectric anisotropy are required for devices based on the deformation of a homeotropically aligned nematic layer,[14] and for 'guest-host' displays with positive contrast.[15,16] Almost all of the known liquid crystals of negative dielectric anisotropy are mono-or-di-cyano-substituted esters,[17-28] and have not been found completely satisfactory for the above mentioned applications. Nematic mixtures containing a recently reported dicyano-substituted ethane appear to satisfy the necessary requirements.[5] As mono cyano-substituted liquid crystals possess lower viscosities than the corresponding dicyano-substituted compounds and often lower melting points,[28] the ethanes (I) containing only one nitrile function (X_2 = CN; R = trans-4-n-alkylcyclohexylmethyl) may be interesting compounds to investigate.

2. RESULTS AND DISCUSSION

A variety of two-ring and three-ring, laterally substituted ethane compounds (1-3) could be produced from the substituted 1-(trans-4-n-alkylcyclohexyl)-2-(4-hydroxyphenyl)ethane prepared according to Reaction Scheme 1. The required trans-4-n-alkylcyclohexane acetic acids could be produced according to modified literature methods.[3] It proved that the overall yields of the desired acids were superior when prepared by cyanation of the corresponding bromo(trans-4-n-alkylcyclohexyl)methanes and subsequent hydrolysis, rather than by direct carbonation of the corresponding Grignard reagent.[3] Hydrogenation of the ketone produced from the Friedels-Crafts reaction utilizing

REACTION SCHEME 1



(1)

(2)

(3)

the corresponding acid chloride, proceeded in equally high yield by use of lithium aluminum hydride or catalysis using palladium on carbon. These remaining steps proceeded with quantitative yields of raw product, except for the cyanation of the bromo-compound, which gave the usual yield of ca. 50 - 65%. The bromo-compound could be prepared as described above or by bromination 1-(trans-4-n-alkylcyclohexyl)-2-(4-hydroxyphenyl)ethane and subsequent alkylation. Both of these reactions gave quantitative yields of pure product. All of these reactions are described in detail in the Experimental section.

The liquid crystal transition temperatures of various compounds (1) are listed in Table 1, and plotted for a homologous series ($n = 5$; $X_1 = F$; $X_2 = H$) against the length of the alkoxy chain (m) in Figure 1. All of the compounds ($X_1 = F$; $X_2 = H$) in Table 1 are of moderately low melting point ($21° < C\text{-}N/I < 46°$) and exhibit monotropic or narrow-range enantiotropic nematic phases ($10° < N\text{-}I < 35°$). The clearing points (N-I) increase generally with increasing length of the alkyl chain (n, 3 → 7).

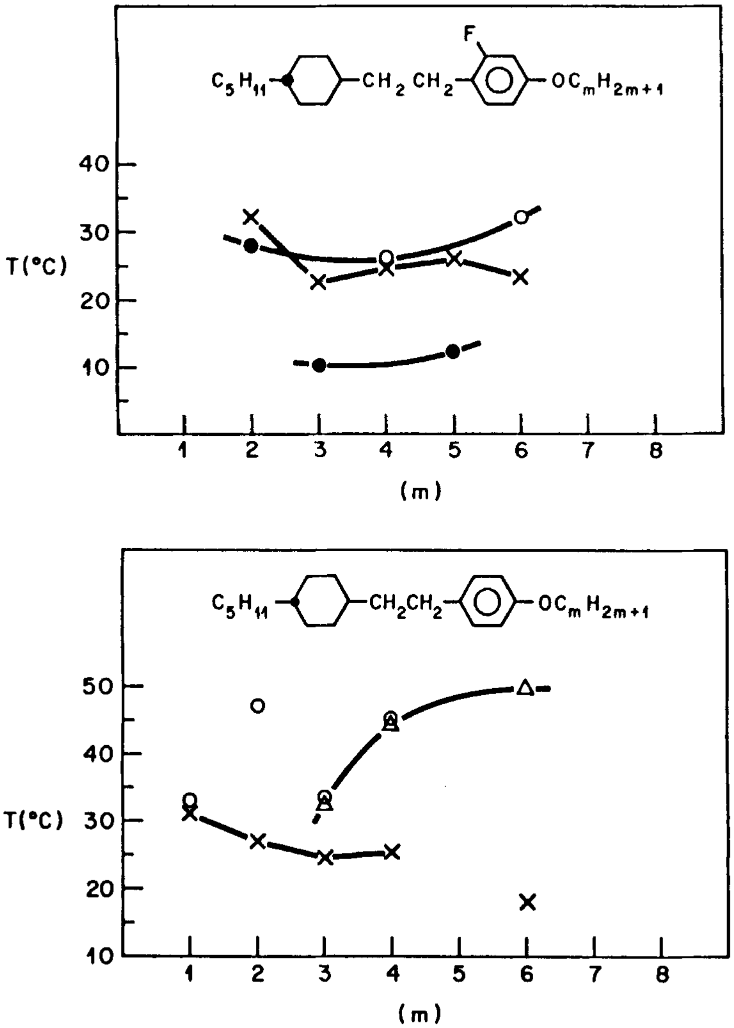
Consistent with standard knowledge[9-13], the smectic-nematic/isotropic liquid transition temperatures of the 2-fluoro-substituted compounds ($X_1 = F$; $X_2 = H$) are significantly lower (more than 60°) than those of corresponding non fluoro-substituted compounds ($X_1 = X_2 = H$)[6]. This is well illustrated by comparison of Figures 1 and 2 where the liquid crystal transition temperatures of the fluoro-substituted and the corresponding non fluoro-substituted ethanes (taken from the literature)[6] are plotted against the number of carbon atoms (m) in the terminal alkoxy chain. Whereas the non fluoro-substituted compounds (eg, $n = 5$; $m = 4$) exhibit high smectic-nematic transition

TABLE 1 Transition temperatures (°C) for compounds of structure 1 (see Reaction scheme)

C_nH_{2n+1}	C_mH_{2m+1}	X_1	X_2	C-N/I	N-I	$\Delta T_{N-I}(X\rightarrow F)$
C_3H_7	C_2H_5	F	H	22	(14)	-19
C_3H_7	C_4H_9	F	H	21	(12)	-21
C_3H_7	C_6H_{13}	F	H	28	(22)	-
C_5H_{11}	C_2H_5	F	H	32	(28)	-19
C_5H_{11}	C_3H_7	F	H	22.5	(10)	-23.5
C_5H_{11}	C_4H_9	F	H	24	26	-19
C_5H_{11}	C_5H_{11}	F	H	26	(12)	-
C_5H_{11}	C_6H_{13}	F	H	23.5	29.5	-20
C_7H_{15}	C_2H_5	F	H	46	(35)	-16
C_7H_{15}	C_4H_9	F	H	31	34	-
C_7H_{15}	C_6H_{13}	F	H	29.5	35	-
C_7H_{15}	CH_3	H	F	32	(29)	-11
C_7H_{15}	C_2H_5	H	F	53	(34)	-
C_7H_{15}	C_6H_{13}	H	F	45	(35)	-

() Denotes a monotropic transition temperature

temperatures (S-N = 44°) and narrow-range nematic phases (N-I = 45°), the corresponding fluoro-substituted compounds (1; n = 5; m = 4) possess only a nematic phase (N-I = 26°; S-N < -20°). The nematic-isotropic transition temperatures are also significantly lower (ca. -17°, on average), see Table 1 and Figures 1 and 2. This decrease is greater than that (ca. -11°, on average) observed for the analogous



FIGURES 1 and 2 Plots of transition temperatures against number of carbon atoms (m) of the ethanes formulated; X, crystal-smectic/nematic transition; Δ, smectic nematic/isotropic transition; O, enantiotropic nematic-isotropic transition; ●, monotropic nematic-isotropic transition.

esters, where the ethyl linkage has been replaced by a carboxyl group.[11]

The liquid crystal transition temperatures of three 3-fluoro-substituted ethanes (X_1 = H; X_2 = F) are given in Table 1. The melting point of one homologue (n = 7; m = 2) is higher (C-I = 53°) than that (C-I = 46°) of the analogous 2-fluoro-substituted compound (X_1 = F; X_2 = H), whereas the clearing points are almost identical (34° and 35°). The corresponding 3-fluoro-substituted esters on the other hand exhibit much lower nematic-isotropic transition temperatures (ca. -15 → -30°) than the corresponding 2-fluoro-substituted esters. This suggests that the 2- and 3-positions of the ethanes (1) are equivalent, whereas they are non equivalent for the esters[10]. This non equivalence may be mainly due to the polarity of the carboxyl central linkage, giving rise to different intramolecular dipole-dipole interactions dependent upon whether the fluorine atom is in the 2- or 3-position.[10]

The values of the dielectric constants and elastic contants of one homologue (n = 5; m = 4) of the ethanes (1) are listed in Table 2. The salient features of these data are the low negative dielectric anisotropy and the relatively low value of the ratio of the bend (k_{33}) and splay (k_{11}) elastic constants. The low values of the dielectric constants (ε_1 and ε_2) are due to the presence of two relatively small dipoles (1.3 D and 1.4 D)[30] attributable to the oxygen and fluorine atoms.

The liquid crystal transition temperatures of three-ring laterally substituted ethanes (2) are recorded in Table 3. The melting and clearing points of the three-ring, 2-fluoro-substituted ethanes (X_1 = F; X_2 = H) exhibit the same trends as the analogous two-ring ethanes (1), ie,

TABLE 2 Physical data for one homologue (n = 5; m = 4; X_1 = F; X_2 = H) of compounds of structure 1 measured at 0.95 x T_{N-I}

Property	Value	Units
ε_1	3.33	
ε_2	3.72	
$\Delta\varepsilon$	-0.39	
k_{11}	10.62	10^{-7}dyne
k_{22}	4.95	10^{-7}dyne
k_{33}	11.72	10^{-7}dyne
k_{33}/k_{11}	1.10	
k_{22}/k_{11}	0.43	

they generally increase with increasing alkyl chain length. However, the addition of a second trans-1,4-disubstituted cyclohexane ring has increased the clearing point (ca. +87°, on average) much more than the melting point (ca. +37°, on average). Thus wide-range, enantiotropic nematic phases (ca. 50°) are observed for several homologues (eg, n = 3; m = 3 and n = 5; m = 3).The smectic-nematic transition temperatures have also been increased dramatically and wide-range, enantiotropic smectic phases (S_A and S_E) are observed for several three-ring homologues with long alkyl chains ($n + m \geq 10$).

The melting point and nematic-isotropic transition temperature of the 3-fluoro-substituted ethane (X_1 = H; X_2 = F; n = 7; m = 3) are approximately equal to those of the corresponding 2-fluoro-substituted ethane (X_1 = F; X_2 = H). The smectic-nematic transition temperature is higher

TABLE 3 Transition temperatures (°C) for compounds of structure 2

C_nH_{2n+1}	C_mH_{2m+1}	X_1	X_2	C-S/N	S_E-S_A	S_A-N/I	N-I
C_3H_7	C_3H_7	F	H	64	-	-	108
C_3H_7	C_5H_{11}	F	H	54.5	-	-	110.5
C_3H_7	C_7H_{15}	F	H	73	73.5	77.5	108
C_5H_{11}	C_3H_7	F	H	61.5	-	-	110
C_5H_{11}	C_5H_{11}	F	H	72	-	73	113
C_5H_{11}	C_7H_{15}	F	H	88	-	94	110
C_7H_{15}	C_3H_7	F	H	45	-	(42)	108
C_7H_{15}	C_3H_7	H	F	50.5	-	90	110
C_7H_{15}	C_3H_7	H	Cl	46	-	(41)	96
C_7H_{15}	C_3H_7	H	CN	57	-	95.5	[90]
C_7H_{15}	C_3H_7	H	Br	44	-	(10)	85.5

() Denotes a monotropic transition temperature

[] Denotes a 'virtual' value for the transition temperature

(ca. +48°) see Table 3.

The effect of lateral substituents (X_1 = H; X_2 = F,Cl,CN,Br) of various sizes on the liquid crystal transition temperatures is shown in Table 3 and Figure 3. Since the cyano-substituted ethane only possesses an enantiotropic smectic phase (see below) a 'virtual' value for the nematic-isotropic transition temperature has been determined by linear extrapolation from a series of binary mixtures with the bromo-substituted compound (see Figure 4 below). A linear inverse relationship between the nematic-isotropic transition temperature and the size of the lateral substituent is observed. This is identical with those results obtained for most laterally substituted compounds of low negative or positive dielectric anisotropy[9,10]. With the exception of the cyano-substituted ethane (see below) the smectic-nematic transition temperature also decreases with increasing size of the lateral substituent. These results seem to confirm the postulation that lateral substituents hinder the parallel alignment between nearest neighbour molecules, thus decreasing the short-range order (and consequently the smectic-nematic/isotropic and the nematic-isotropic transition temperatures).[9,10] It is interesting to note that despite the almost equal size of the bonded bromine and cyano-functions (2.6Å and 2.5Å) the bromo-substituted ethane exhibits a wide-range enantiotropic nematic phase (C-N = 44°; N-I = 85.5°) and only a strongly monotropic smectic phase (S_A-N = 10°)), while the cyano-substituted ethane only possesses an enantiotropic smectic phase (C-S_A = 57°; S_A-I = 95.5°). The major difference between these two compounds are the values of the dipole moment of the bonded bromine atom (1.5. D) and the nitrile function (4.0 D) and this suggests that the smectic-nematic/isotropic transition temperature is dependent on such strong dipole moments not parallel to the long axis of the molecule. Similar results have been observed for a number of benzoate esters, [2,20] some of which also incorporated an ethyl linkage. The dielectric anisotropy of the bromophenyl ethane (2; X_1 = H; X_2 = Br) is slightly negative (-0.8 at 0.98 x T_{N-I}). The dielectric anisotropy of the corresponding cyanophenyl compound (2; X_1 = H; X_2 = CN) as extrapolated from a binary nematic mixture with the bromophenyl ethane (60 mol%) was found to be significantly

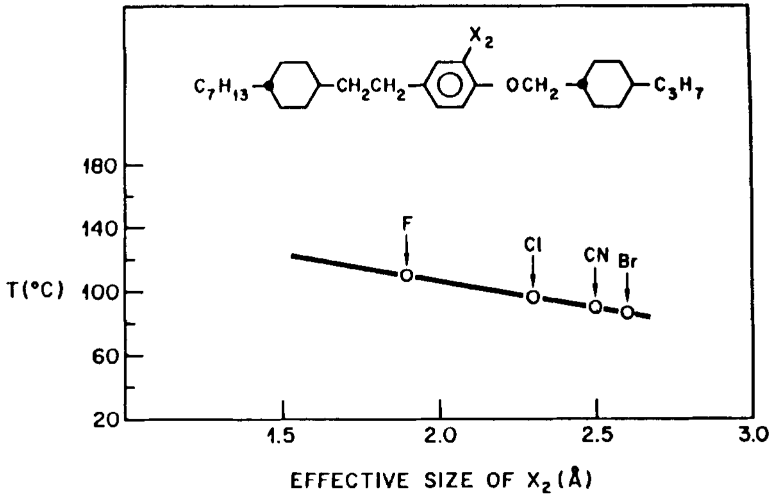


FIGURE 3 Plot of the nematic-isotropic liquid transition temperatures (°) against the size of the lateral substituent X_2 of the ethanes formulated.

more negative (-3.5 at 0.98 x T_{N-I}) as would be expected due to the large dipole moment of the nitrile function.

The liquid crystal transition temperatures of some novel esters (3) are listed in Table 4. The transition temperatures of ester derivatives (3; X_1 = F; X_2 = H) are generally higher than those of the corresponding ethers (2; X_1 = F; X_2 = H). However, the nematic-isotropic transition temperatures are increased (ca. +32°, on average) more than either the melting points (ca. + 13°, on average) or the smectic-nematic transition temperatures (ca. +10°, on average). Thus several homologues (eg, n = m = 3;

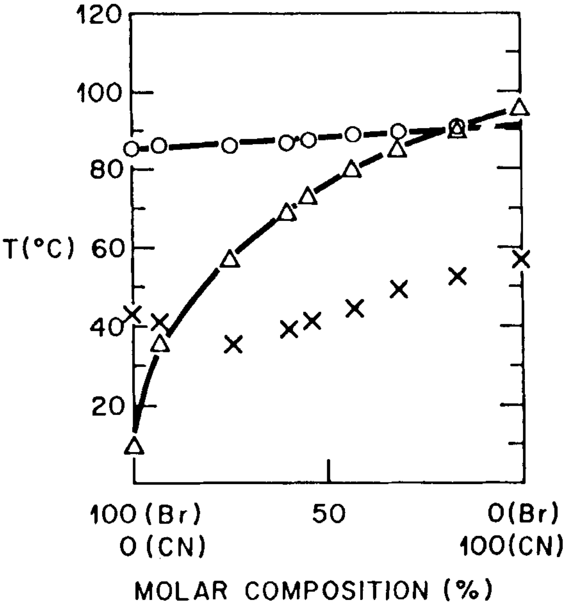


FIGURE 4 Plot of the transition temperatures against the composition of binary mixtures of the bromo- and cyano-substituted ethanes (2; X_1 = H; X_2 = Br and X_1 = H; X_2 = CN), see Figure 7 and 2 for the meaning of the symbols used.

n = 3; m = 5) possess wide-range enantiotropic nematic phases (> 75°), cf. the three-ring ethers (2; > 50°). The esters (3; eg, n = 3; m = 5) exhibit much lower (ca. -100°) smectic-nematic transition temperatures (S_A-N $\leq$ 25°) than those of the corresponding non fluoro-substituted esters (S_A-N $\cong$ 125°),[7] while the nematic-isotropic transition temperatures are only marginally lower (ca. -15°). The dielectric anisotropy of one of the esters (3; n = m = 5) has been determined (-0.7 at 0.85 x T_{N-I}).

TABLE 4 Transition temperatures (°C) for compounds of structure 3

C_nH_{2n+1}	C_mH_{2m+1}	X_1	X_2	$C\text{-}S_A/N$	$S_A\text{-}N$	N-I
C_3H_7	C_3H_7	F	H	72	-	140
C_3H_7	C_5H_{11}	F	H	68	-	146.5
C_3H_7	C_7H_{15}	F	H	84	91	140
C_5H_{11}	C_3H_7	F	H	65	-	141
C_5H_{11}	C_5H_{11}	F	H	72.5	(72)	147
C_5H_{11}	C_7H_{15}	F	H	100	111	142

() Denotes a monotropic transition temperature

3. EXPERIMENTAL

3.1 Transition Temperatures

The liquid crystal transition temperatures (± 0.1°C) of the ethanes (1-3) recorded in Tables 1, 3 and 4, were determined by optical microscopy using a Leitz Orthoplan microscope in conjunction with a Mettler FP52 heating stage and FP5 control unit. When necessary, the Mettler stage could be cooled (< -20°C) by allowing nitrogen gas, cooled by liquid nitrogen, to pass through the stage at a controlled rate. The 'virtual' nematic isotropic liquid transition temperature of the cyano-substituted ethane (2), was determined in the usual manner.[32]

3.2 Purity

The purity of the compounds was determined by thin layer chromatography (TLC) and gas chromatography (GLC). A Perkin Elmer Sigma 1 gas chromatographic system and also a Perkin Elmer 3920B gas chromatograph with a Hewlett Packard 3380A integrator were used.

3.3 Structure

The structure of the compounds were checked by analysis of their ^{1}H-nmr, infra-red, and mass spectra; the instruments used were a Brucker WP 200 nmr spectrometer, a Perkin Elmer PE 683 infra-red spectrometer with a model 3600 data station, and a Hitachi RMU 6L mass spectrometer, respectively. Combustion analysis was also carried out.

3.4 Physical Properties

The physical properties of the ethanes reported in Table 2 and in the text were determined using methods previously reported[31]

3.5 Synthetic Details

2-Fluoro-4-methoxy-α-(trans-4-pentylcyclohexyl)acetophenone (X_1 = F; X_2 = H). A solution of trans-4-pentylcyclohexyl acetyl chloride (13.0 g, 0.057 mol) prepared in the usual way, and 3-fluoroanisole (8.6 g, 0.068 mol) in sieve-dried dichloromethane (30 cm^3) was added dropwise to a mixture of anhydrous aluminum chloride (9.8 g, 0.074 mol) and sieve-dried dichloromethane (30 cm^3) under anhydrous conditions and cooled *via* an ice-bath. The mixture was stirred overnight and allowed to attain room temperature. The reaction solution was added to a small volume of 15% hydrochloric acid and stirred for *ca.* 20 min. The organic layer was separated off and the aqueous layer was shaken with chloroform (2 x 40 cm^3). The combined organic layers were washed with water (2 x 500 cm^3) and dried ($MgSO_4$). After crystallization from hexane at 0° pure (99%) 2-fluoro-4-methoxy-α-(*trans*-4-pentylcyclohexane)acetophenone was obtained (13.3 g, 73.4%) mp 71-72°, m/e, 320.

C 74.96	H 9.12%	F 5.93%	(Required)
C 71.71%	H 9.06%	F 5.21%	(Found)

Results for the other homologues were: *propyl* (X_1 = F; X_2 = H), m/e, 292, 39.5%, mp 75-76°; *heptyl* (X_1 = F; X_2 = H), m/e, 348, 42%, 49-50°; *heptyl* (X_1 = H; X_2 = F), m/e, 348, 50%, mp 75-76°; *heptyl* (X_1 = H; X_2 = Cl), m/e, 364, 366, 68%, mp 80 - 81°; *heptyl* (X_1 = H; X_2 = Br), m/e, 408, 410, 62.5%, mp 81-82°; *heptyl* (X_1 = X_2 = H), m/e, 330, 54.5%, mp 55-56°.

1-(4-trans-Pentylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl) ethane (X_1 = F; X_2 = H). - A solution of 2-fluoro-4-methoxy-α-(*trans*-4-pentylcyclohexyl)acetophenone (10 g, 0.031 mol) in sieve-dried chloroform (70 cm^3) was added dropwise to a stirred solution of aluminum lithium hydride (2.1 g, 0.056 mol) and anhydrous aluminum chloride (15 g, 0.113 mol) in sodium-dried ether (70 cm^3). The resultant mixture was heated under reflux overnight. After decomposition of the complex and excess of hydride in the normal way, the organic layer was separated off and the aqueous layer was shaken with ether (2 x 100 cm^3). The combined organic layers were washed with brine (2 x 500 cm^3) and dried ($MgSO_4$). The solvent was removed under partially reduced pressure to yield crude product (9.0 g, 94%) m/e, 306, which was used without further purification in the next reaction.

Results for the other homologues were: <u>propyl</u> (X_1 = F; X_2 = H), m/e, 278, 92%; <u>heptyl</u> (X_1 = F; X_2 = H), m/e, 334, 97%; <u>heptyl</u> (X_1 = H; X_2 = F), m/e, 334, 96%; <u>heptyl</u> (X_1 = H; X_2 = Cl), m/e, 350, 352, 95%; <u>heptyl</u> (X_1 = H; X_2 = Br), m/e, 394, 396, 94%; <u>heptyl</u> (X_1 = X_2 = H), m/e, 316, 96%.

<u>1-(4-trans-Pentylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl) ethane</u> (X_1 = F; X_2 = H). - A mixture of 2-fluoro-4-methoxy-<u>α</u>-(<u>trans</u>-4-pentylcyclohexyl)acetophenone (1.8 g, 0.0056 mol), palladium on carbon (10%; 0.8 g) and ethyl acetate (50 cm^3) was stirred at room temperature under an atmosphere of dry hydrogen for <u>ca.</u> 5 hrs, when the uptake of hydrogen was complete. The mixture was filtered to remove the catalyst and the resultant solution evaporated down under reduced pressure to yield raw product (1.6 g, 93%) m/e, 306, which was used without further purification in the next step.

<u>1-(4-trans-Pentylcyclohexyl)-2-(2-fluoro-4-hydroxyphenyl) ethane</u> (X_1 = F; X_2 = H). - A solution of 1-(4-<u>trans</u>-pentylcyclohexyl)-2-(2-fluoro-4-methoxyphenyl)ethane (9.0 g, 0.029 mol) in sieve-dried dichloromethane (100 cm^3) was added dropwise to a solution of boron tribromide (11.0 g,

0.044 mol) in sieve-dried dichloromethane (100 cm^3) under anhydrous conditions and cooled *via* an ice-bath. The reaction was stirred overnight and allowed to obtain room temperature. The reaction was poured carefully onto water (500 cm^3) and shaken. The organic layer was separated off and the aqueous layer shaken with dichloromethane (2 x 50 cm^3). The combined organic layers were washed with water (2 x 1000 cm^2) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the resultant residue was crystallized from hexane at 0° to yield pure (99.9%) phenol (8.5 g, 98%) mp 78-78°, m/e, 292.

C 78.04%	H 10.00%	F 6.50%	(Required)
C 78.28%	H 9.86%	F 6.36%	(Found)

Results for other homologues were: *propyl* (X_1 = F; X_2 = H), m/e, 264, 90.5%, mp 74.5 - 75.5°; *heptyl* (X_1 = F; X_2 = H), m/e, 320, 92%, mp 80 - 81°; *heptyl* (X_1 = H; X_2 = F), m/e, 320, 94%, mp 70 - 71°; *heptyl* (X_1 = H; X_2 = Cl), m/e, 336, 338, 88%, mp 56 - 57°; *heptyl* (X_1 = H; X_2 = Br), m/e, 380, 382, mp 50 - 51°; *heptyl* (X_1 = X_2 = H), m/e, 302, 82%, mp 95 - 96°.

1-(4-trans-Heptylcyclohexyl)-2-(3-bromo-4-hydroxyphenyl) ethane. (X_1 = H; X_2 = Br) A solution of bromine (0.7 g, 0.0038 mol) in sieve-dried dichloromethane (20 cm^3) was added dropwise to a solution of 1-(4-*trans*-heptylcyclohexyl)-2-(4-hydroxyphenyl)ethane (1.15 g, 0.0038 mol) in sieve-dried dichloromethane (20 cm^3) under anhydrous conditions and cooled via an ice-bath. The reaction solution was stirred for 1 hr. at 0° and then added to water (200 cm^3). The organic layer was separated off and the aqueous layer shaken with chloroform (2 x 50 cm^3). The combined organic layers were washed with saturated sodium bicarbonate solution (2 x 100 cm^3), with water (2 x 500 cm^3) and dried ($MgSO_4$). After removal of the solvent, the crude product (quantitative yield) was crystallized from hexane to yield pure (98%) phenol (1.0g, 69%), mp 50 - 51°, m/e, 380, 382.

1-(4-trans-Pentylcyclohexyl)-2-(2-fluoro-4-butyloxyphenyl) ethane (X_1 = F; X_2 = H). - A mixture of 1-(4-trans-pentylcyclohexyl)-2-(2-fluoro-4-hydroxyphenyl)ethane (1.0 g, 0.0037 mol), 1-bromobutane (0.8 g, 0.0055 mol), anhydrous potassium carbonate 1.9 g, 0.0137 mol) and sieve-dried butanone (30 cm^3) was heated under reflux overnight under anhydrous conditions. The reaction mixture was added to water (250 cm^3) and shaken with chloroform (3 x 50 cm^3). The combined organic layers were washed with water (2 x 500 cm^3) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the crude product was eluted down a silica-gel column using hexane as eluent. Single-spot fractions were collected and evaporated down together. The residue was distilled in a short-path distillation apparatus to yield pure product (0.9 g, 75.5%) m/e, 348, see Table 1 for the liquid crystal transition temperatures of this two-ring ether and other homologues (1) prepared similarly. The three-ring ethers (2) were synthesized in the same way except that they were purified by crystallization from ethyl acetate until constant transition temperatures were obtained, see Table 3.

C 79.2%	H 10.70%	F 5.45%	(Required)
C 79.08%	H 10.68%	F 5.62%	(Found)

4-(trans-4-Pentylcyclohexyl)ethyl-2-fluorophenyl trans-4-pentylcyclohexyl-1-carboxylate (X_1 = F; X_2 = H). - A solution of *trans*-4-pentylcyclohexane-1-carboxyl chloride (0.65 g, 0.0031 mol prepared in the usual way) in sodium-dried toluene (10 cm^3) was added to a solution of 1-*trans*-4-pentylcyclohexyl)-2-(2-fluoro-4-hydroxyphenyl)ethane (0.9g, 0.0031 mol), sieve-dried pyridine (2 cm^3) and sodium-dried toluene (10 cm^3) under anhydrous conditions. The resultant solution was stirred overnight and added to cold, dilute hydrochloric acid and extracted with chloroform (3 x 50 cm^3). The combined organic layers were washed with water (2 x 500 cm^2) and dried ($MgSO_4$). The filtered solution was evaporated and the residue taken up in a minimum of solvent and eluted down a silica-gel column using a 1:1 mixture of toluene and hexane as eluent. Single-spot fractions containing the ester were combined and evaporated down together to yield the desired product, which was crystallized from ethyl acetate until constant transition temperatures were observed (see Table 4 for the liquid crystal transition temperatures of this ester and the other esters (3) prepared by this method. The yield of crude product was quantitative).

4. CONCLUSIONS

A variety of stable laterally substituted ethanes of weak-to-moderate negative dielectric anisotropy have been synthesized. The large majority of these new compounds exhibit enantiotropic nematic phases, the two-ring ethanes just at, or above, room temperature and the three-ring ethanes at much higher temperatures (100-150°). The usual linear inverse relationship between the size of the lateral substituent and the nematic-isotropic transition temperature has been established. The smectic-nematic transition temperatures of these laterally substituted ethanes are generally much lower than those of the analogous ethanes bearing a hydrogen atom instead of the lateral substituent. One cyanophenyl substituted ethane has been synthesized and found to be of moderately strong negative dielectric anisotropy (< -3.5). This compound only possesses a smectic phase but homologues with shorter alkyl chain lengths might be expected to exhibit an enantiotropic nematic phase.

ACKNOWLEDGEMENTS

Mr. F. Rime is thanked for very competent technical assistance. The authors are also grateful to Professor R. Tabacchi and Dr. S. Claude of the Institut de Chimie, Neuchâtel, for the ^{1}H nmr and mass spectral data and Dr. Eder of the Institut de Microchemie, Geneva, for the combustion analyses.

REFERENCES

1. D. COATES and G.W. GRAY, J. Chem. Soc. Perkin II, 863 (1976).
2. NGUYEN HUU TINH, A. ZANN, and J.C. DUBOIS, Mol. Cryst. Liq. Cryst., 53, 29 (1979); 53, 43 (1979).
3. G.W. GRAY and D.G. McDONNEL, Mol. Cryst. Liq Cryst., 53, 147 (1979); N. CARR, G.W. GRAY, and D.G.McDONNELL, Mol. Cryst. Liq. Cryst. 97, 13 (1983).

4. M.J. BRADSHAW, J. CONSTANT, D.G. McDONNELL, and E.P. RAYNES, Mol. Cryst. Liq. Cryst. 97, 177 (1983).
5. M. SCHADT, Japan Display '83, 220 (1983); M. SCHADT, M. PETRZILKA, P.R. GERBER, A. VILLIGER, and G. TRICKES, Mol. Cryst. Liq. Cryst. 94, 139 (1983).
6. R. ROLAND, A. VILLIGER, and E. WIDMER, German Patent Application, 320 1721 (1981); M. PETRZILKA, German Patent Application 322 6051 (1981); M. PETRZILKA and M. SCHADT, German Patent Application, 323 7367 (1982).
7. H. TAKATSU, K. TAKEUCHI, and H. SATO, Japan Display '83, 228 (1983).
8. M.A. OSMAN and T. HUYNH-BA, Mol. Cryst. Liq. Cryst. Lett., 82, 339 (1983).
9. G.W. GRAY, in Advances in Liquid Crystals, Vol. 2, edited by G.H. Brown (Academic Press, London, 1976), p. 1 - 72, and references contained therein.
10. G.W. GRAY and S.M. KELLY, Mol. Cryst. Liq. Cryst. 75, 109 (1981).
11. G.W. GRAY, C. HOGG, and D. LACEY, Mol. Cryst. Liq. Cryst., 67, 1 (1981).
12. J. CONSTANT and E.P. RAYNES, Mol. Cryst. Liq. Cryst. 70, 105 (1981).
13. R. EIDENSCHINK, Mol. Cryst. Liq. Cryst., 94, 119 (1983); R. EIDENSCHINK and M. ROEMER, Proceedings of the 13th Freiburger Arbeitstagung Flüssigkristalle, (1983).
14. Hp. SCHAD, SID-Digest, 244 (1982); F.J. KAHN, Appl. Phys. Lett., 20, 199 (1972); M.F. SCHIEKEL and K. FAHRENSCHON, Appl. Phys. Lett., 19, 391 (1971).
15. G.H. HEILMEIER and L.A. ZANONI, Appl. Phys. Lett., 13, 91 (1968); D.L. WHITE and G.N. TAYLOR, J. Appl. Phys., 45, 4718 (1974).
16. T.J. SCHEFFER, Phil. Trans. R. Soc. Lond. A 309, 189 (1983); T. UCHIDA and M. WADA, Mol. Cryst. Liq. Cryst. 63, 19 (1981).
17. R. STEINSTRAESSER, German Patent Application 224 0864 (1972).
18. P.V. ADOMENAS, Russian Patent Application USSR 562547 (1975).
19. D. ERDMANN, R. EIDENSCHINK, J. KRAUSE, and L. POHL, German Patent Application 261 3293 (1976).
20. J.C. DUBOIS, A. ZANONI, and A.B. BEGUIN, Mol. Cryst. Liq. Cryst., 42, 139 (1977); J.C. DUBOIS and A.B. BEGUIN, Mol. Crystl. Liq. Cryst., 47, 193 (1978).
21. A.B. BEGUIN, J.C. DUBOIS, and A. ZANONI, German Patent Application 283 5662 (1978).

22. A.B. BEGUIN, A. ZANONI, and J.C. DUBOIS, German Patent Application 283 6086 (1978).
23. R. EIDENSCHINK, J. KRAUSE, and L. POHL, German Patent Application 285 3728 (1978).
24. T. INUKAI, K. FURUKAWA, H. INOUE, and K. TERASHIMA, Mol. Cryst. Liq. Cryst. 94, 109 (1983).
25. M.A. OSMAN, European Patent Application EPA 002 3728 (1979).
26. M.A. OSMAN and T. HUYNH-BA, Mol. Cryst. Liq. Cryst. 82, 293 (1983); 92, 57 (1983).
27. T. HUYNH-BA, S.M. KELLY, and M.A. OSMAN, European Patent Application EPA 008 5995 (1983).
28. T. HYUNH-BA and S.M. KELLY, Helv. Chim Acta, 66, 1850 (1983); Swiss Patent Application CH 4805/82 (1982).
29. CRC Handbook of Chemistry and Physics, edited by R.C. WEAST(CRC Press, Florida, 1981-1982).
30. A.L. McCLELLAN, Tables of Experimental Dipole Moments, (Freeman, San Francisco, 1963).
31. Hp. SCHAD and M.A. OSMAN, J. Chem. Phys., 75, 880 (1981).
32. G.W. GRAY and S.M. KELLY, J. Chem. Soc. Perkin II, 26 (1981).