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Synthesis and some Physical Properties of Phenylpyrimidines†

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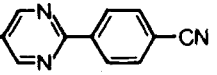
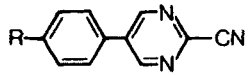
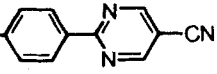
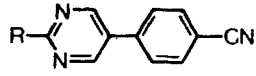
The four classes of 2,5-disubstituted cyano-alkylphenyl- and alkyl-cyanophenyl-pyrimidines have been prepared.

I 

III 

II 

IV 

Their synthesis is discussed and procedures are given for the preparation of a member of each class.

Compounds I and II are nematic. They have a positive anisotropy of the dielectric constants which have been measured and are compared with those of Schiff' bases and esters. Some comparative viscosity measurements have also been carried out.

INTRODUCTION

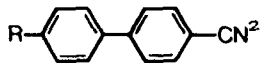
Recent interest in field effect displays based on the twisted nematic effect[1] led to a growing demand for liquid crystals with a positive dielectric anisotropy. Such compounds are usually obtained when a molecule has a functional group with a strong dipole moment parallel to the molecular axis.

The discovery of the alkyl- and alkoxy-cyanobiphenyls[2] (Table I) is one of the most promising developments in the field of liquid crystals. Strong positive dielectric anisotropy, low viscosity, and mesomorphic ranges near room temperature make these compounds very attractive as

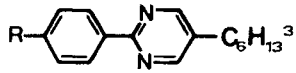
† Presented at the Sixth International Liquid Crystal Conference, Kent State University, August 1976.

TABLE I

Transition temperatures (°C) of 4′-alkyl- and 4′-alkoxy-4-cyanobiphenyls[2] and of 5-hexyl-2-(4-alkoxyphenyl)-pyrimidines[3]



R	mp.	smect.–nem.	clp.
n-C_4H_9—	46.5°	—	(16.5°)
n-C_5H_{11}—	22.5°	—	35°
n-C_6H_{13}—	13.5°	—	27°
n-C_7H_{15}—	28.5°	—	42°
n-C_8H_{17}—	21°	32.5°	40°
n-$C_5H_{11}O$—	53°	—	67.5°
n-$C_6H_{13}O$—	58°	—	76.5°
n-$C_7H_{15}O$—	53.5°	—	75°
n-$C_8H_{17}O$—	54.5°	67.5°	80°



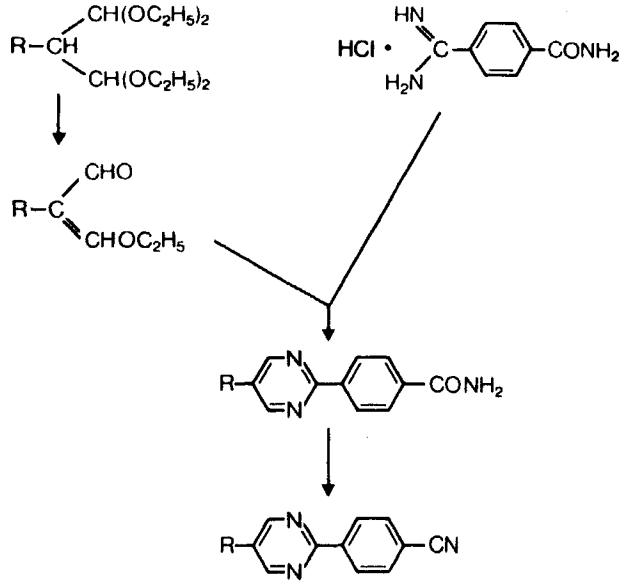
n-$C_5H_{11}O$—	42°	—	53.5°
n-$C_6H_{13}O$—	31°	—	60.5°
n-$C_7H_{15}O$—	35°	—	58.5°

Value in parenthesis indicates monotropy.

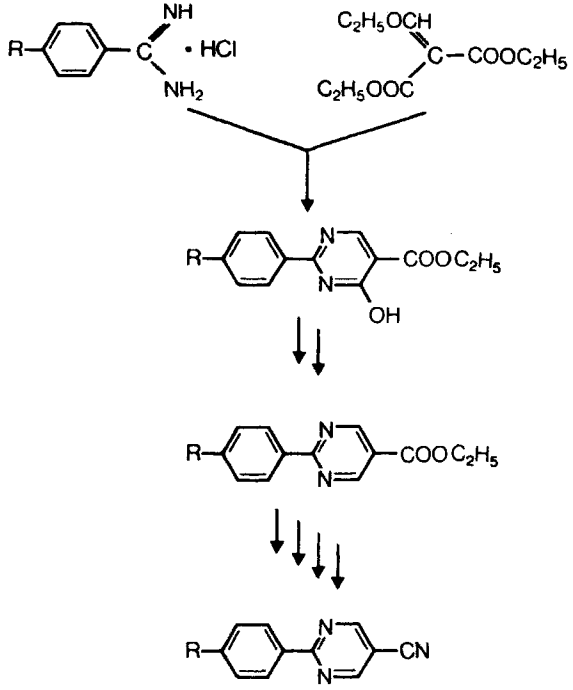
components of mixtures for field effect displays. Another class of compounds with a positive dielectric anisotropy, alkoxyphenyl alkylpyrimidines (Table I) has been described by Zaschke.[3] In this case the major contribution to the dipole moment parallel to the molecular axis comes from the pyrimidine part. Pyrimidine[4] alone has a dipole moment of 2.0 D, which is small compared with the 4 D of the cyano group in benzonitrile.[4] However, in both cases, the direction of the dipole moment is well defined and strictly parallel to the molecular axis. Combination of these two groups in the four classes of cyano alkyl phenylpyrimidines described in the present paper should have interesting aspects because no significant dipole moment perpendicular to the molecular axis is present.

PREPARATION OF MATERIALS

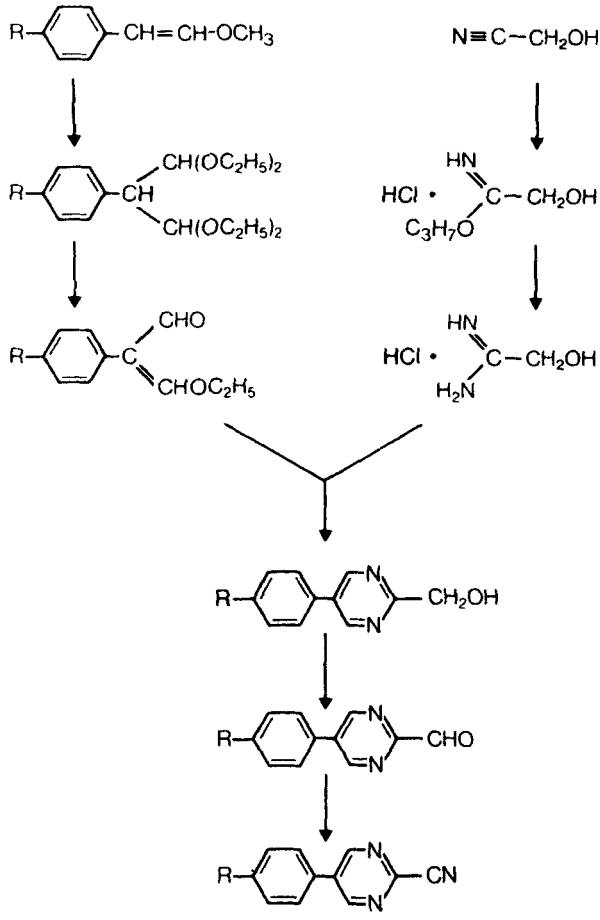
In all four classes the synthesis of the pyrimidine moiety makes use of an amidine hydrochloride and a derivative of a β-dicarbonyl compound. For the introduction of the cyano group three different methods were used. The reaction sequences are outlined in Schemes 1–4. Experimental procedures



SCHEME 1 Synthesis of 5-alkyl-2-(4-cyanophenyl)-pyrimidines (Class I)



SCHEME 2 Synthesis of 5-cyano-2-(4-alkylphenyl)-pyrimidines (Class II)

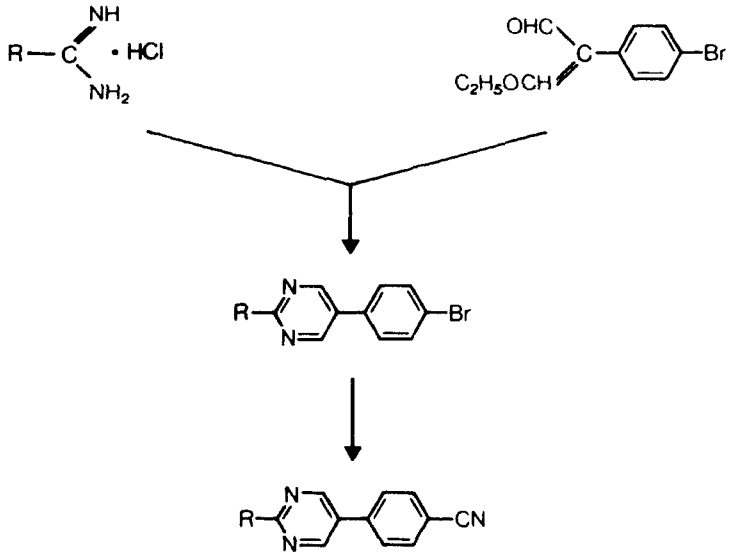


SCHEME 3 Synthesis of 2-cyano-5-(4-alkylphenyl)-pyrimidines (Class III)

are given for a representative member of each class. All compounds were recrystallized to constant melting point. Melting- and clearing points were determined with a Mettler hot stage FP52 and a Mettler FP5 electronic recording apparatus. Mass spectra were recorded on a MS 9 AEI (Manchester) and NMR spectra on a Varian EM 360 spectrometer ($CDCl_3$, TMS).

Preparation of 5-Hexyl-2-(4-cyanophenyl)-pyrimidine (Class I, Scheme I)

30.4 g of 2-hexylmalondialdehyde tetraethylacetal[5] are stirred in 40 ml of ethanol with 3.6 ml of water and 3 drops of concentrated sulfuric acid at



SCHEME 4 Synthesis of 2-alkyl-5-(4-cyanophenyl)-pyrimidines (Class IV)

50°C under nitrogen for 18 hours. The mixture is diluted with ether and the 2-hexylmalondialdehyde formed as a by-product is extracted with diluted sodium carbonate solution. Concentration of the ether phase gives 2-hexyl-3-ethoxyacrolein which is used in the next step without purification.

A suspension of 16.5 g of 4-amidinobenzoic acid amide hydrochloride,[6] 15 g of 2-hexyl-3-ethoxyacrolein and 7.5 g of sodium methylate in 150 ml of methanol is stirred over night at room temperature under nitrogen. The precipitate which is formed is filtered, washed with water, methanol, and ether, and dried. 17.9 g of 4-(5-hexylpyrimidin-2-yl) benzoic acid amide, melting point 231.5–233°C, are obtained.

A suspension of 15.6 g of amide described above are refluxed and stirred for 90 minutes in a mixture of 350 ml of ethylene chloride and 5.6 ml of phosphorous oxychloride. The mixture is diluted with ether, washed with 2 *N* sodium hydroxide and then with water until neutral. The organic phase is dried and evaporated to give 14.6 g of 5-hexyl-2-(4-cyanophenyl)-pyrimidine. After chromatography on 100 g of silica gel in benzene a product with a melting point of 54.5°C and a monotropic clearing point of 38.5°C is obtained.

NMR δ 0.7–2.0 ppm (m, 11), 2.7 (t, 2, J = 7 Hz), 7.5–7.8 (m, 2), 8.3–8.6 (m, 2), 8.65 (s, 2); mass spectrum m/e (%) 265 (M^+, 61), 208 (26), 195 (58), 194 (100), 167 (18), 39 (25). $C_{17}H_{19}N_3$: calc. C 76.95, H 7.22, N 15.83, found C 76.80, H 7.34, N 15.80.

Preparation of 5-Cyano-2-(4-heptylphenyl)-pyrimidine (Class II, Scheme 2)

2-(4-Heptylphenyl)-4-chloro-5-pyrimidine carboxylic acid ethyl ester (m.p. 49.5°C) is obtained from 4-heptylbenzamidine hydrochloride[7] and ethoxymethylene malonic acid diethyl ester[8] with sodium ethylate in ethanol and subsequent treatment of the 2-(4-heptylphenyl)-4-hydroxy-5-pyrimidine carboxylic acid ethyl ester with phosphorous oxychloride according to A. R. Todd and F. Bergel.[9]

13.4 g of 2-(4-heptylphenyl)-4-chloro-5-pyrimidine carboxylic acid ethyl ester are hydrogenated with 1.1 g of palladium carbon (5%) and 5.6 g of anhydrous potassium acetate in 156 ml of ethanol at room temperature until uptake of 1 mole of hydrogen. The catalyst is filtered off and after evaporation, starting material present is removed by chromatography on silica gel with methylene chloride as eluant to give 11 g of crude product. After distillation (b.p. 130°C/0.01 mm) the colourless ethyl 2-(4-heptylphenyl)-5-pyrimidine carboxylate has a melting point of 89°C.

10.5 g of this ethyl ester is hydrolyzed with 15.2 g of sodium hydroxide in 100 ml of water and 20 ml of ethanol by refluxing for 1 hour. After cooling, the mixture is acidified with 80 ml of 20% of hydrochloric acid. The precipitated acid is filtered, washed, and dried. 9.6 g of crude 2-(4-heptylphenyl)-5-pyrimidine carboxylic acid are refluxed with 50 ml of thionyl chloride for 2 hours, cooled, and concentrated. Traces of thionyl chloride are removed by dissolving the residue in toluene followed by concentration. The crude acid chloride is dissolved in 100 ml of anhydrous dioxane and added with stirring to 200 ml of anhydrous dioxane saturated with ammonia at room temperature. Ammonia is bubbled through the mixture for 4 hours and a colourless precipitate is formed. After standing over night, the reaction mixture is concentrated *in vacuo*, the residue stirred with 100 ml of water, separated, washed with water and dried to give a crude yield of 9.3 g. Sublimation of a sample gives 2-(4-heptylphenyl)-5-pyrimidine carboxylic acid amide with a melting point of 251–251.5°C (dec.).

9.1 g of 2-(4-heptylphenyl)-5-pyrimidine carboxylic acid amide are refluxed in 100 ml of phosphorous oxychloride for 2 hours. Excess reagent is distilled *in vacuo* and traces are removed by addition of toluene and subsequent concentration. The residue is purified by chromatography on silica gel. Elution with methylene chloride and methylene chloride/2% acetone gives 7.2 g of product. After recrystallization from ether/hexane and distillation at 125°C (0.01 mm) 7.4 g of 5-cyano-2-(4-heptylphenyl)-pyrimidine with a melting point of 96–96.5°C and a clearing point of 109°C are obtained.

NMR δ 0.7–1.8 ppm (m, 13), 2.65 (t, 2, J = 7 Hz), 7.2–7.45 (m, 2), 8.3–8.55 (m, 2) 9.0 (s, 2); mass spectrum m/e (%) 279 (M^+, 46), 208 (15), 195 (82), 194

(100), 43 (20). $C_{18}H_{21}N_3$: calc. C 77.38, H 7.58, N 15.04, found C 77.39, H 7.54, N 15.08.

In the same manner as discussed above 5-cyano-2-(4-alkoxyphenyl)-pyrimidines (class II) are prepared using 4-alkoxybenzamidine hydrochlorides as starting materials.

Preparation of 5-Cyano-2-(4-pentanoyloxyphenyl)-pyrimidine (Class II, Table 4)

2-(4-Hydroxyphenyl)-4-hydroxy-5-pyrimidine carboxylic acid ethyl ester (m.p. 264.5–268°C) is obtained from 4-hydroxybenzamidine hydrochloride and ethoxymethylene malonic acid diethyl ester[8] with sodium ethylate in ethanol.[9] Subsequent acetylation with acetic anhydride/pyridine at 100°C gives 2-(4-acetoxyphenyl)-4-hydroxy-5-pyrimidine carboxylic acid ethyl ester, m.p. 229.5–230.5°C.

With this acetate, the reaction with phosphorous oxychloride[9] and the steps described in the preceding chapter can be carried out with moderate to good yields.

1.9 g of 5-cyano-2-(4-acetoxyphenyl)-pyrimidine (m.p. 167–168°C) are stirred with 1.9 g of potassium carbonate in 380 ml of ethanol and 38.5 ml of water at room temperature for 4 hours. After acidification, the mixture is filtered from by-products, concentrated, the residue thoroughly washed with water and dried. A sublimed sample of 5-cyano-2-(4-hydroxyphenyl)-pyrimidine has a melting point of 257–259°C. 0.79 g of the crude product is dissolved at 0°C in 20 ml of pyridine and approximately 1 ml of pentanoyl chloride are added. After stirring at room temperature over night, ice and hydrochloric acid are added and the product is extracted with ethyl acetate. Adsorption on 40 g of silica gel, elution with benzene and recrystallization from acetone/hexane gives 0.9 g of colourless crystals. A sublimed sample of 5-cyano-2-(4-pentanoyloxyphenyl)-pyrimidine has a melting point of 114°C and a clearing point of 119.5°C.

NMR δ 0.75–2.05 ppm (m, 7), 2.6 (t, 2, J = 7 Hz), 7.1–7.4 (m, 2), 8.35–8.65 (m, 2) 8.95 (s, 2); mass spectrum m/e (%) 281 (M^+, 3), 197 (100), 119 (20), 85 (38), 57 (50). $C_{16}H_{15}N_3O_2$: calc. C 68.31, H 5.37, N 14.94, found C 68.36, H 5.28, N 15.05.

Preparation of 2-Cyano-5-(4-propylphenyl)-pyrimidine (Class III, Scheme 3)

114 g of anhydrous glycolic acid nitrile and 120 g of propanol are cooled to 0°C and 53 g of dry hydrogen chloride are added within 4 hours. After an additional hour at room temperature the white precipitate is filtered, washed with ether and dried. 153.5 g of the 243 g of product obtained are

now dissolved in 700 ml of anhydrous methanol and 410 ml of a 4.1 *N* ammonia solution in methanol are added at 10°C in 15 minutes. After addition of 500 ml of ether, ammonium chloride is removed by filtration. Further dilution with ether gives now a precipitate of 2-hydroxyacetamidine hydrochloride, which is filtered and dried (53 g).

23 g of 4-propylphenylmalondialdehyde tetraethylacetal[5] are dissolved in 60 ml of ethanol, 2.1 ml of water and four drops of concentrated sulfuric acid (95–97%), stirred over night at 50°C, diluted with ether and extracted with 2*N* sodium hydroxide solution. 13.1 g of crude 2-(4-propylphenyl)-3-ethoxyacrolein, obtained from the ether phase, are added at 15°C to a suspension of 26.5 g of 2-hydroxyacetamidine hydrochloride in a solution of 6.62 g of sodium in 400 ml of methanol. The mixture is stirred over night at room temperature, then diluted with ether and washed with water to give 12.5 g of crude 5-(4-propylphenyl)-2-pyrimidine methanol. A sample treated with charcoal and recrystallized twice from acetone/hexane has a melting point of 92.5–93°C.

11.2 g of 5-(4-propylphenyl)-2-pyrimidine methanol are dissolved in 150 ml of toluene. Three portions of 25 g of manganese dioxide are added successively. After each addition the mixture is refluxed for one hour. After filtration and concentration 9.2 g of crude 5-(4-propylphenyl)-2-pyrimidine carboxaldehyde are obtained. Chromatography on silica gel gives a sample with a melting point of 110–111°C.

To 8.4 g of crude 5-(4-propylphenyl)-2-pyrimidine carboxaldehyde dissolved in 26 ml of anhydrous pyridine, 2.6 g of hydroxylamine hydrochloride are added at room temperature. A slight temperature increase is observed and the mixture is stirred for 1½ hours. After addition of 3.9 g of phosphorous oxychloride an exothermic reaction starts to give an inside temperature of 150°C. Without external cooling, the mixture is stirred for approximately one hour, and, now at room temperature, diluted with ether. The organic phase is washed with water, dried and concentrated. 7.4 g of crude product are purified by chromatography on 700 g of silica gel in benzene. 5.1 g of pure 2-cyano-5-(4-propylphenyl)-pyrimidine are obtained with a melting point of 119–119.5°C.

NMR δ 0.95 ppm (t, 3, J = 7 Hz), 1.35–2.05 (m, 2), 2.7 (t, 2, J = 7 Hz), 7.2–7.65 (AA'BB', 4) 9.0 (s, 2); mass spectrum m/e (%) 223 (M^+, 30) 194 (100), 115 (12). $C_{14}H_{13}N_3$: calc. C 75.31, H 5.87, N 18.82, found C 75.37, H 5.96, N. 18.74.

Preparation of 2-Heptyl-5-(4-cyanophenyl)-pyrimidine (Class IV, Scheme 4)

7.5 g of 4-bromophenylmalondialdehyde tetraethylacetal[5] in 20 ml of ethanol are stirred at 50°C overnight with 1 ml of water and 2 drops of

concentrated sulfuric acid (96%). The reaction mixture is concentrated *in vacuo*, diluted with ether and washed with 3 *N* sodium hydroxide and water. 2.3 g of crude 2-(4-bromophenyl)-3-ethoxyacrolein are obtained which are dissolved in a solution of 0.6 g of sodium in 40 ml of anhydrous methanol. 1.6 g of octanoic acid amidine hydrochloride[10] are added and the mixture is refluxed over night, diluted with water and 3 *N* hydrogen chloride, and extracted with ether. 2.8 g of crude product after recrystallization from ethyl acetate give 0.9 g of 2-heptyl-5-(4-bromophenyl)-pyrimidine with a melting point of 71–72.5°C. Additional material is obtained by chromatography on silica gel with hexane/ether 4 : 1.

3 g of recrystallized 2-heptyl-5-(4-bromophenyl)-pyrimidine and 4.6 g of cuprous cyanide are refluxed in 75 ml of dimethylformamide over night. After cooling, the mixture is stirred with 50 ml of a 10% aqueous solution of ethylene diamine and then extracted with ether. The organic phase is again washed with an ethylene diamine solution and then thoroughly with water. The crude product is purified by chromatography on 250 g of silica gel with hexane/ether 4 : 1. 1.1 g of pure 2-heptyl-5-(4-cyanophenyl)-pyrimidine, recrystallized from hexane, has a melting point of 89.5–90°C.

NMR δ 0.65–2.15 ppm (m, 13), 3.05 (t, 2, J = 7 Hz), 7.5–7.9 (AA'BB', 4) 8.85 (s, 2); mass spectrum m/e (%) 279 (M^+, 16), 251 (5), 237 (4), 236 (5), 222 (12), 208 (35), 195 (100), 127 (13). $C_{18}H_{21}N_3$: calc. C 77.38, H 7.58, N 15.04, found C 77.17, H 7.70, N 15.03.

Preparation of 5-(4'-Cyanophenyl)-2-(4'-alkylphenyl)-pyrimidines (Table V)

These compounds are easily accessible from intermediates obtained in the synthesis of class II and IV. Detailed experimental procedures will be described in a forthcoming publication.

MESOMORPHIC AND PHYSICAL PROPERTIES

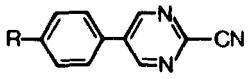
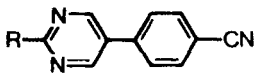
Mesomorphic Properties

In classes III and IV (Table II) with the nitrogen atoms of the pyrimidine ring in 3,5-positions relative to the ring junction, we were not able to observe mesomorphic properties. The melting points are high and since these compounds crystallize readily, only limited supercooling is possible.

Compared with the cyano alkyl biphenyls (Table I), the clearing points of the members of class I (Table III) are slightly higher. However, due to a large rise of the melting points, the mesomorphic ranges are considerably smaller.

TABLE II

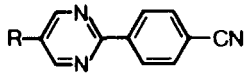
Melting points (°C) of 2-cyano-5-(4-alkylphenyl)-pyrimidines and 2-alkyl-5-(4-cyanophenyl)-pyrimidines.

R	mp.	mp.
n-C_3H_7—	119–119.5°	—
n-C_4H_9—	114–115°	91–91–5°
n-C_5H_{11}—	108–108.5°	87–87.5°
n-C_6H_{13}—	104°	76–77°
n-C_7H_{15}—	106.5–107°	89.5–90°

TABLE III

Transition temperatures (°C) of 5-alkyl-2-(4-cyanophenyl)-pyrimidines



R	mp.	clp.
n-C_4H_9—	61–61.5°	—
n-C_5H_{11}—	70.5–71°	(52°)
n-C_6H_{13}—	54.5°	(38.5°)
n-C_7H_{15}—	44.5–45°	51°
n-C_8H_{17}—	66–66.5°	(47°)

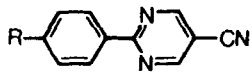
Values in parenthesis indicate monotropy.

Compounds of class II (Table IV) have unexpectedly high clearing points. The mesomorphic ranges are comparable with or larger than those of the corresponding biphenyls (Table I). The smectic properties are more pronounced. A smectic phase appears with a hexyl- and a hexoxy-substituent. In the biphenyl series this is the case only with the octyl- and octoxy-compound.

The 5-cyanophenyl-2-alkylphenyl-pyrimidines of Table V have very large mesomorphic ranges. They are promising components for mixtures with high clearing points. We have also prepared positional isomers with respect to the ring nitrogens. These results will be presented in detail in a subsequent publication.

TABLE IV

Transition temperatures (°C) of 5-cyano-2-(4-alkylphenyl)-pyrimidines, 5-cyano-2-(4-alkoxyphenyl)-pyrimidines, and 5-cyano-2-(4-alkanoyloxyphenyl)-pyrimidines

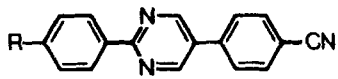


R	mp.	smect.–nem.	clp.
n-CH_3—	205.5°	—	—
n-C_2H_5—	146.5–147°	—	—
n-C_3H_7—	126°	—	(106.5°)
n-C_4H_9—	108.5–109°	—	(101.5°)
n-C_5H_{11}—	96°	—	109°
n-C_6H_{13}—	86.5°	101.5°	102.5–103°
n-C_7H_{15}—	96.5°	109°[a]	—
n-CH_3O—	174.5–175°	—	—
n-C_2H_5O—	152.5–153°	—	(149.5°)
n-C_3H_7O—	146.5°	—	(137°)
n-C_4H_9O—	119–120°	—	139.5°
n-$C_5H_{11}O$—	98°	—	133°
n-$C_6H_{13}O$—	93.5°	121°	134°
n-$C_7H_{15}O$—	102.5°	127°	129.5°
n-C_4H_9COO—	114°	—	119.5°
n-$C_5H_{11}COO$—	108–108.5°	—	123°
n-$C_6H_{13}COO$—	109°	—	119°

Values in parenthesis indicate monotropy.
[a] Smectic–isotropic clearing point.

TABLE V

Transition temperatures (°C) of 5-cyanophenyl-2-alkylphenyl-pyrimidines



R	mp.	clp.
n-C_2H_5—	167–167.5°	279–279.5°
n-C_3H_7—	167°	278.5°
n-C_4H_9—	138.5°	266–266.5°
n-C_5H_{11}—	131.5°	262–263°
n-C_6H_{13}—	121.5–122°	250–250.5°
n-C_7H_{15}—	121.5°	245°

Dielectric Constants

The static dielectric constants were measured at a frequency of 1592 Hz using a Wayne-Kerr B 642 autobalance bridge. A parallel plate capacitor with stainless steel electrodes separated by 1 mm Teflon spacers served as a sample holder. The temperature of the samples was measured with a platinum resistor mounted directly in one of the electrodes thus providing good thermal contact with the sample. A magnetic field of 6 kG was used to align the liquid crystal molecules perpendicular or parallel to the electrode surfaces. The apparatus used was similar to the one described earlier.[11]

The viscosity measurements were made using a rotating cone Brookfield microviscosimeter. The bulk viscosity η thus measured gives a good indication of at least the relative viscous behaviour of different liquid crystals.[12]

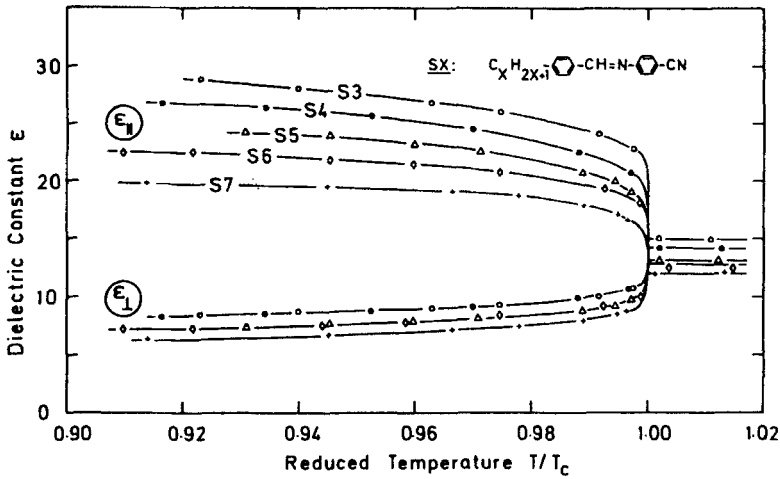


FIGURE 1 Temperature dependence of the dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ of five alkyl cyano Schiff' bases SX.

Figures 1–4 show measurements of the static dielectric constants $\varepsilon_\perp$ and $\varepsilon_\parallel$ of nematic alkyl cyano Schiff' bases, alkyl cyano esters and various cyanophenyl pyrimidines on reduced temperature T/T_c (T and T_c in °K). All compounds investigated exhibit a large positive dielectric anisotropy $\Delta\varepsilon = (\varepsilon_\parallel - \varepsilon_\perp)$.

A common feature of the data depicted in Figures 1–4 is the decrease of $\Delta\varepsilon$ with increasing length of the hydrocarbon chains within a homologous series. A similar dependence of $\Delta\varepsilon$ on chain length was found earlier in the homologous series of cyano alkoxy Schiff' bases.[11,13] The measured decrease of $\Delta\varepsilon$ is partly due to the decreasing molecular density $N = \rho N_A/M$ with

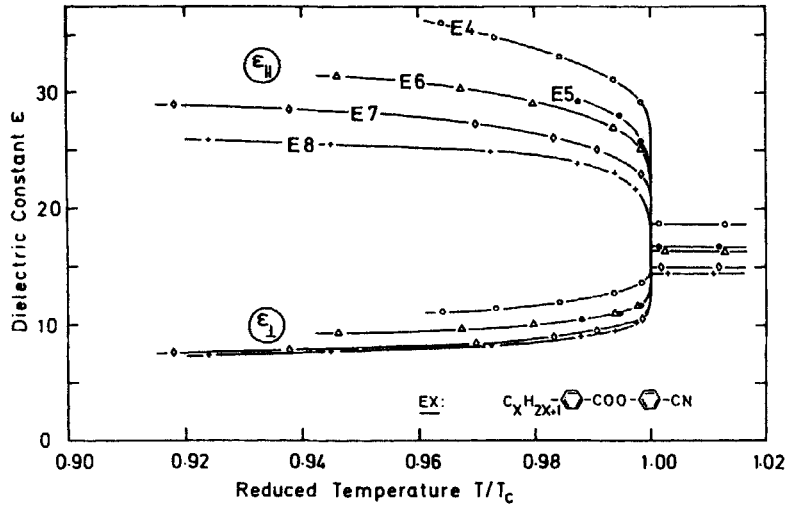


FIGURE 2 Temperature dependence of the dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of five alkyl cyano esters EX.

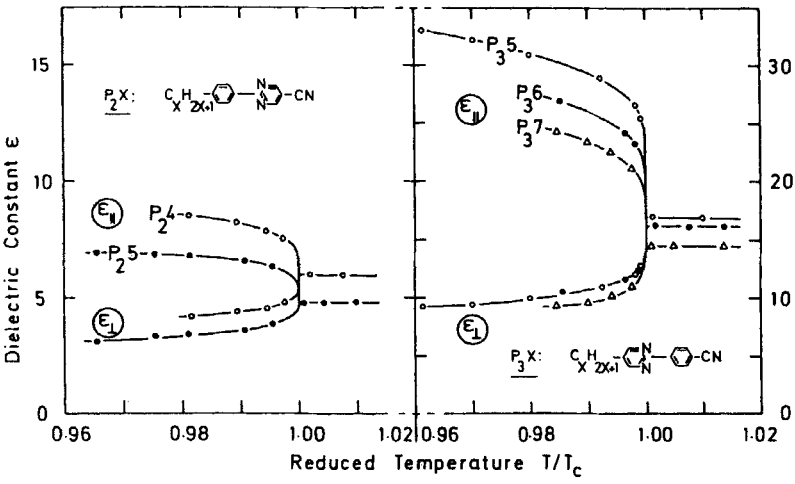


FIGURE 3 Temperature dependence of the dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of 5-alkyl-2-(4-cyanophenyl)-pyrimidines P_3X (Class I) and 5-cyano-2-(4-alkylphenyl)-pyrimidines P_2X (Class II).

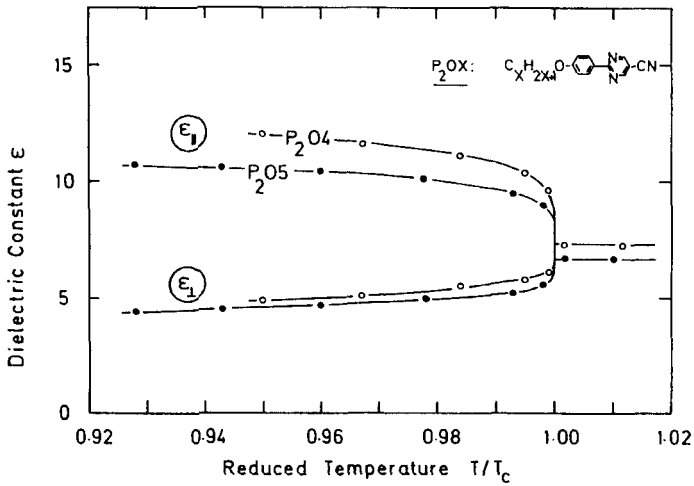


FIGURE 4 Temperature dependence of the dielectric constants $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of two 5-cyano-2-(4-alkoxyphenyl)-pyrimidines P_2OX (Class II).

increasing chain length which follows from the expression for the dielectric anisotropy derived by Maier and Meier.[14]

$$\frac{\Delta\varepsilon}{4\pi} = NhF\left[\Delta\alpha - F\frac{\mu^2}{2kT}(1 - 3\cos^2\beta)\right]S. \tag{1}$$

N_A = Avogadro's number, ρ = density, M = molecular weight, h = cavity field factor of the empty cavity, F = reaction field factor, $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ = anisotropy of induced polarizability, μ = permanent dipole moment, β = angle between μ and the long molecular axis, and $S = \langle 1 - \frac{3}{2}\sin^2\theta\rangle$ = long range order parameter.[15] Apart from depending on molecular density the decrease of $\Delta\varepsilon$ might also depend on possible changes of short-range anti-parallel dipole correlation of the permanent dipole moments[16] $\mu_{\parallel}$ leading to a decrease of $\varepsilon_{\parallel}$ with increasing chain length. If this were so then one would expect also an increase of $\varepsilon_{\perp}$,[17] which was not the case (Figures 1–4). However, the measured decrease of $\varepsilon_{\perp}$ with increasing chain length was considerably smaller than that of $\varepsilon_{\parallel}$, and in some cases $\varepsilon_{\perp}$ stayed even constant [c.f. $\varepsilon_{\perp}$(S3) $\simeq$ $\varepsilon_{\perp}$(S4) and $\varepsilon_{\perp}$(S5) $\simeq$ $\varepsilon_{\perp}$(S6) in Figure 1].

The large positive dielectric anisotropy of the components studied (Figures 1–4) is due mainly to the contributions of the strong permanent dipole moments of the cyano end group, the ester linkage and/or the pyrimidine groups to the total parallel dipole moment of the respective molecules. This is also shown by the increase of $\Delta\varepsilon$ with decreasing temperature (Figures 1–4) which is qualitatively in agreement with the S/T-dependence of the dipolar part of Eq. (1).

TABLE VI

Dielectric anisotropy $\Delta\varepsilon = (\varepsilon_{\parallel} - \varepsilon_{\perp})$, nematic to isotropic transition temperature T_c and molecular weight M of cyano compounds belonging to different classes of nematic liquid crystals and having the same number of atoms in their side chains. The dielectric data were measured at constant reduced temperature $T/T_c = 0.98$.

[a]	$\Delta\varepsilon$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	T_c(°C)	M
S (X = 5)	13.2	21.6	8.4	75.0	276.4
E (X = 5)	20.0	30.2	10.2	56.5	293.4
K15[2]	8.3	16.5	8.2	35.0	249.4
P_3 (X = 5)	21.3	31.3	10.0	52.0	251.3
P_2 (X = 5)	3.4	6.8	3.4	109.0	251.3
P_2O (X = 4)	7.0	12.5	5.5	139.5	253.3
P_2OCO (X = 4)[b]	3.0	8.4	5.4	119.5	281.3

[a] For abbreviations see Figures 1–4.
[b] For abbreviations see Table 4.

In Table VI data of $\Delta\varepsilon$ are depicted, which are obtained from measurements made at the same reduced temperature $T/T_c = 0.98$ (Figures 1–4)—i.e. at constant long range order parameter S[15]—with compounds belonging to different classes but having the same number of carbon atoms in their hydrocarbon chain. For comparison the dielectric data of the alkyl cyano biphenyl[2] K15 are also included. The data in Table VI give only a crude estimate of the dependence of $\Delta\varepsilon$ on molecular structure. A more adequate correlation would require to take into account the molecular weight M as well as additional information on either the polarizability α or the dipole moments μ (c.f. equation 1). However, the measurements in Figures 1–4 and the $\Delta\varepsilon$ values depicted in Table VI show that the pyrimidines† P_3X—together with the esters[18] EX and to a lesser extent the Schiff' bases[19] SX—are among those nematic liquid crystals exhibiting largest positive dielectric anisotropy. In the case of P_3X the large $\Delta\varepsilon$ is due to the additivity of the pyrimidine dipole moment and the dipole moment of the cyano end group to the total dipole moment along the molecular axis. The considerably smaller dielectric anisotropies of the cyano pyrimidines P_2X, P_2OX and P_2OCOX (Figures 3 and 4, Table VI) are mainly due to the subtractive effect of the pyrimidine dipole moment with respect to the cyano dipole moment.

Bulk Viscosity

The measurements depicted in Figure 5 show the dependence of bulk viscosity η on temperature for S7, E7, P_37 and K21 all of which have the same alkyl chain length. The activation energies of the four components are very similar (Figure 5), thus allowing to extrapolate η (T) of P_37 into the nematic

† For this and the following abbreviations see Figures 1–4.

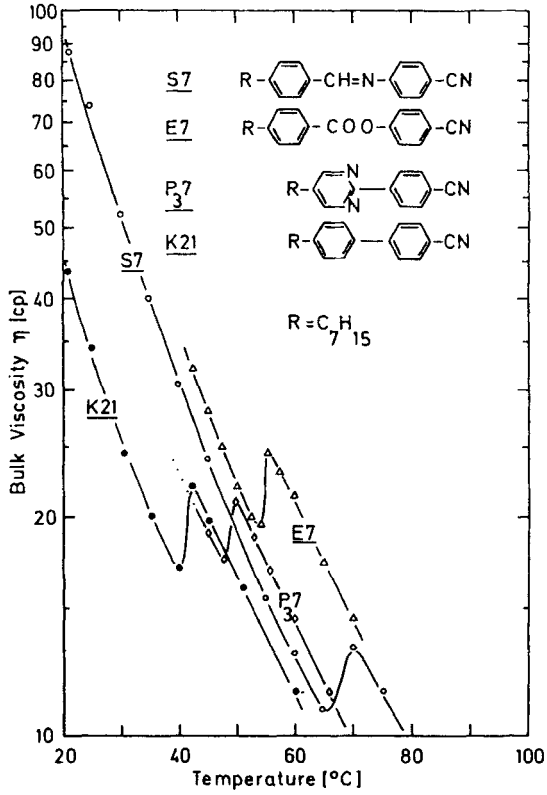


FIGURE 5 Temperature dependence of the bulk viscosity of four liquid crystalline cyano-compounds having the same alkyl chain length and belonging to different classes of liquid crystals; i.e. Schiff' bases, esters, phenylpyrimidines and biphenyls.

range of K21 (dotted curve in Figure 5). The measurements made at 38°C (Figure 5) then show that E7 is the most viscous component ($\eta = 40$ cp) followed by S7 ($\eta = 33$ cp), $P_3 7$ ($\eta = 25$ cp) and K21 ($\eta = 16$ cp).

The increase of bulk viscosity at the nematic to isotropic transition temperature (Figure 5) is due to its increase from $\eta_2 < \eta < \eta_3$, η_1 in the nematic phase[12] to $\eta \simeq \eta_3$ in the isotropic phase; η_1 η_2 and η_3 = viscosity coefficients.

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