Synthesis and Mesomorphic Properties of Diphenyl- and Biphenylpyrimidines

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The synthesis and mesomorphic properties of four classes of cyano-substituted diphenyl- and biphenylpyrimidines are reported. The new compounds are colourless, chemically and photochemically stable and have wide mesomorphic ranges. The synthesis of one member of each homologous series is described in detail.

The use of 2,5-disubstituted pyrimidine rings as a structural element in liquid crystals is well known. Mono- and disubstituted diphenylpyrimidines have been studied mainly by Schubert *et al.* [1–3] and more recently various phenylpyrimidines have been prepared by Zäschke [4]. Only minor changes of the molecular geometry are expected when a phenyl group in a given liquid crystalline structure is replaced by a pyrimidine ring. However, we have shown in a recent publication [5] that a strong influence on the dielectric properties can be demonstrated. In cyano-alkylphenyl- and alkyl-cyano-phenylpyrimidines the relative position of the permanent dipole moments of the pyrimidine and the cyano group is very important in determining the size of the dielectric constants. A large positive dielectric anisotropy [5] is obtained if the contributions are additive (see 2). On the other hand, much smaller dielectric anisotropies [5] due to the subtractive effect are observed when the two dipole moments have opposite directions (see 1).

In view of the fact that there is still great interest in liquid crystalline materials with a positive anisotropy of the dielectric constants, we decided to prepare four homologous series of diphenyl- and

biphenylpyrimidines. Their synthesis is outlined in Schemes 1–4. 4-Substituted benzamidine hydrochlorides have been used as the nitrogen containing units for the construction of the pyrimidine ring. In series 1 (Scheme 1), condensation with diethyl ethoxymethylene-malonate forms a hydroxy-pyrimidine carboxylate. The hydroxy-group is removed by substitution with chlorine [6] and subsequent catalytic reduction. For the preparation of series 2–4 (Schemes 2–4), a substituted malonic dialdehyde tetraacetal is used as precursor, obtained from enol-esters by treatment with ethyl orthoformate and boron trifluoride etherate [7]. After partial hydrolysis to the relatively unstable substituted ethoxy-acrolein, a smooth condensation with a benzamidine in methanol or ethanol and sodium alkoxide takes place [5, 7]. The cyano group is introduced either by substitution of bromine with cuprous cyanide or by dehydration of the amide with phosphorous oxychloride. The synthesis of one member of each homologous series is described in detail in the experimental part.

All transition temperatures which are listed in Table I have been determined by differential thermal analysis with an accuracy of at least $\pm 0.2^\circ\text{C}$. Corresponding values usually within 1°C have also been observed by microscopic determination. Only for clearing points at temperatures over 250°C were differences of several degrees sometimes found, microscopic observation always giving the higher value. In many samples differential thermal analysis gave broad, poorly defined exothermic peaks around 200°C in the first melting process. When subsequently the sample was cooled, recrystallized and measured again, these peaks no longer appeared. Table I lists also the heats of melting, which, unless otherwise stated were always measured with recrystallized samples. The accuracy of the instrument is better than $\pm 5\%$.

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Table I. Transition temperatures and heats of melting of diphenyl- and biphenylpyrimidines.

R	m.p. [°C] ^a	Additional transitions [°C]	clp. [°C]	ΔH_m [kcal/mole]
1				
C ₂ H ₅	(72.5) 166.5	241	290 ^b	3.1
C ₃ H ₇	140.5	234	289.5 ^b	4.2
C ₄ H ₉	(99.5) 126.5	216.5	274.5	2.6
C ₆ H ₁₃	(90.5) 134.5	154 ^c , 160.5 ^c , 217.5	258	3.2
2				
C ₂ H ₅	182	—	262.5	5.3
C ₃ H ₇	153.5	—	259	5.4
C ₄ H ₉	93.5	—	244	4.2
C ₅ H ₁₁	125	—	241	6.3
C ₆ H ₁₃	(82.5) 92	193.5	230.5	5.1
C ₇ H ₁₅	103.5	208.5	226.5	5.8
C ₃ H ₇ O	132	—	279.5 ^b	5.2
C ₄ H ₉ O	(110) 119	—	271.5	5.8
C ₅ H ₁₁ O	(82) 91.5 ^d	199	261	6.6 ^d
C ₆ H ₁₃ O	95	226	254.5	6.6
3				
H	(206.5) 219.5	—	—	8.9
C ₂ H ₅	166	180.5	277	4.6
C ₃ H ₇	(69.5) 166	180	276	4.8
C ₄ H ₉	(69.5) 138	180	263	3.8
C ₅ H ₁₁	131.5	176	261.5	4.1
C ₆ H ₁₃	(91.5) 121.5	164	247.5	3.8
C ₇ H ₁₅	(103.5) 121	146.5, 150 ^e	242	3.9
4				
C ₃ H ₇	125.5	214	275.5	4.2
C ₄ H ₉	112	212.5	262	3.8
C ₅ H ₁₁	124	204.5	259.5	6.0
C ₆ H ₁₃	(95) 108	215	246	6.0
C ₇ H ₁₅	(72) 78 ^g	109 ^f , 221.5	241.5	— ^f

^a Values in parentheses refer to transitions between solid modifications. They do not appear after recrystallization.

^b Sublimation and partial decomposition occur during microscopic examination.

^c These transitions cannot be observed by polarizing microscopy.

^d Values obtained by first heating. After recrystallization: m.p. 86 °C and ΔH_m 3.8 kcal/mole.

^e A broad poorly defined transition between 144 and 151 °C is observed by microscopic examination.

^f After recrystallization a new, additional peak appears at 89.5 °C. No ΔH_m could be determined.

^g This transition may be mistaken for the melting point; however, the low ΔH_m of 1.2 kcal/mole suggests that it is a smectic-smectic transition.

Comparison of the clearing points of the four series shows a striking similarity for the series 3 and 4. Corresponding values for the isomers with the same length of the alkyl side chain differ with one exception by only 1 °C or less. The clearing points of series 1 are higher by an average of 12 °C,

those of series 2 lower by approximately 17 °C. A similar dependence of the mesomorphic properties on the relative positions of the pyrimidine nitrogens and the terminal substituents has been observed in monosubstituted diphenylpyrimidines [1] and in phenylpyrimidines [5]. — Only the lower members of the homologous series 2 have a uniform mesomorphic range. Based on texture and low viscosity it has been identified as being nematic. No efforts have been made to determine the other phases.

The new materials described in this paper have high clearing points. Combined with an often relatively low melting point, some of the compounds have mesomorphic ranges as large as 150 °C and compare favourably with 4'-alkyl-4-cyano-*p*-terphenyls found by Gray *et al.* [8]. They will be valuable components for mixtures with high clearing points and a positive anisotropy of the dielectric constants.

Experimental

All compounds were recrystallized to constant melting point and identified by their mass, NMR and infrared spectra. Elemental analysis for C, H and N always gave satisfactory values. Transition temperatures and heats of melting were measured with a Mettler TA 2000 thermoanalyzer system which was also used for the determination of the purity by the cryoscopic method. It was found that all compounds listed in Table I were more than 99% pure. For the microscopic determination of the transition temperatures in polarized light, a Mettler hot stage FP 52 and a Mettler FP 5 electronic recording apparatus was used. Mass spectra were recorded on a MS 9 (AEI, Manchester) spectrometer (ionizing voltage: 70 V; ion source temperature: approx. 250 °C). For NMR spectra, a Varian EM 360 spectrometer (CDCl₃, TMS) was used.

5-Cyano-2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine (1, R = C₆H₁₃, Scheme 1)

Dry hydrogen chloride is passed into a solution of 5.0 g of 4'-*n*-hexyl-4-cyanobiphenyl [9] in 3.8 ml of absolute ethanol and 4.8 ml of absolute benzene for 8 hours while stirring and cooling to 0 °C and the mixture is left to stand overnight at room temperature. After evaporation *in vacuo*, the mixture is treated with 100 ml of absolute ether and 4'-*n*-hexyl-4-biphenyl-imidoethyl ether hydrochloride is isolated by filtration. This crude salt is suspended in 7.6 ml of absolute ethanol and stirred for 40 h with 10.7 g of a 16% (g/g) solution of ammonia in ethanol. The clear solution is evaporated *in vacuo* and the residue is treated with 100 ml of absolute ether. 4'-*n*-Hexyl-4-biphenyl-amidine hydrochloride is isolated by filtration. A mixture of

Scheme 1. Synthesis of 5-cyano-2-(4'-alkyl-4-biphenyl)-pyrimidines.

6.0 g of 4'-*n*-hexyl-4-biphenyl-amidine hydrochloride and 4.9 g of diethyl ethoxymethylene-malonate [10] is stirred in a sodium ethylate solution (obtained from 0.867 g of sodium and 80 ml of ethanol) for 40 min at room temperature and for 40 min under reflux. The yellow mixture is then evaporated *in vacuo* and the residue suspended in 95 ml of water and acidified with 15 ml of glacial acetic acid. Filtration, washing with water and drying yields crude ethyl 2-(4'-*n*-hexyl-4-biphenyl)-4-hydroxypyrimidine-5-carboxylate which can be purified by sublimation at 185 °C in a high vacuum; m.p. 218.0 °C.

6.95 g of this hydroxypyrimidine are boiled for 1 h under reflux with 50 ml of phosphorus oxychloride. The excess reagent is evaporated off *in vacuo* and the residue is chromatographed in methylene chloride on silica gel 60. Elution with methylene chloride and methylene chloride/2% acetone yields ethyl 2-(4'-*n*-hexyl-4-biphenyl)-4-chloro-pyrimidine-5-carboxylate which can be purified by distillation at 180 °C in a high vacuum; m.p. 91.6–91.9 °C; clp. 112.6–112.7 °C.

6.2 g of chloropyrimidine are suspended in 300 ml of ethanol and hydrogenated in the presence of 0.4 g of 5% palladium-on-charcoal and 2.17 g of anhydrous potassium acetate at room temperature until 1 mole of hydrogen has been absorbed. The catalyst is separated and rinsed with methylene chloride and the evaporation residue is dissolved in benzene, diluted with an equivalent amount of

hexane and chromatographed on silica gel 60. Elution with hexane/benzene (1:1) and benzene initially yields a small amount of starting material and then ethyl 2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine-5-carboxylate. This carboxylate can be purified by distillation at 180 °C in a high vacuum; m.p. 129.2 °C; clp. 181 °C.

5.12 g of ethyl 2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine-5-carboxylate are boiled under reflux for 3 h with 150 ml ethanol and 6.1 g sodium hydroxide in 45 ml of water and the mixture is evaporated *in vacuo*. 50 ml of water and 100 ml of 20% hydrochloric acid are added to the residue. Filtration, washing with water and drying yields 2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine-5-carboxylic acid which can be converted into the acid chloride by boiling for 2 h with 30 ml of thionyl chloride. The excess reagent is removed *in vacuo* and the residual acid chloride is suspended in 60 ml of absolute dioxane and added while stirring to a solution of 80 ml of dioxane saturated with ammonia at room temperature. Ammonia is passed into the mixture for a further 4 h and the mixture is left to stand overnight at room temperature. The mixture is then evaporated to dryness and the residue is stirred for 30 min with 100 ml of water, filtered, rinsed with water and dried. There is thus obtained colourless 2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine-5-carboxylic acid amide which can be purified by sublimation at 205 °C in a high vacuum; m.p. 260 °C.

4.31 g of 2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine-5-carboxylic acid amide are boiled for 2 h under reflux with 75 ml of phosphorus oxychloride and the excess reagent is removed *in vacuo*. Toluene is then added and the mixture is concentrated twice *in vacuo*. The residue is taken up in methylene chloride and chromatographed on silica gel 60. Elution with methylene chloride/2% acetone yields 5-cyano-2-(4'-*n*-hexyl-4-biphenyl)-pyrimidine which is purified by recrystallization from acetone/hexane and distillation at 180 °C in a high vacuum; m.p. 134.5 °C; clp. 258 °C.

NMR δ 0.7, 1.95 ppm (11, m), 2.67 (2, t, $J = 7$ Hz), 7.23, 7.55 (4, centers of AA'BB'-spectrum), 7.68, 8.33 (4, centers of AA'BB'-spectrum), 8.93 (2, s); mass spectrum m/e (%) 341 (M, 49), 270 (100), 165 (7), no other peak larger than 5%.

C₂₃H₂₃N₃

Calcd	C 80.91	H 6.79	N 12.31,
Found	C 80.79	H 6.80	N 12.18.

5-(4-*n*-Pentylphenyl)-2-(4-cyanophenyl)-pyrimidine (2, R = C₅H₁₁, Scheme 2)

Dry hydrogen chloride is passed into a solution of 88.6 g of methyl 4-cyanobenzoate in 190 ml of benzene and 170 ml of methanol for 3 h at 0 °C while stirring. The mixture is left to stand for 5 days at +5 °C and the precipitated imido ether hydrochloride is then filtered off. 178 g of the crude product are suspended in 300 ml of methanol and

Scheme 2. Synthesis of 5-(4-alkylphenyl)-2-(4-cyanophenyl)pyrimidines.

after cooling to about -40°C , treated with 130 g of liquid ammonia and the mixture is shaken in an autoclave for 24 h at $+70^{\circ}\text{C}$. After cooling the mixture to room temperature and evaporation of the ammonia, the crystallized product is filtered off and the crystals are washed with hexane and dried overnight at 50°C under a waterpump vacuum, there being obtained 4-amidino-benzoic acid amide hydrochloride.

46.07 g of 1-(4-*n*-pentylphenyl)-2-methoxyethylene [11] are added dropwise to a solution of 2 ml of boron trifluoride etherate in 500 ml of ethyl *ortho*-formate, cooled in an ice bath, and the mixture is then further stirred at room temperature. After dilution with ether, extraction with 1 N sodium hydroxide solution and water and evaporation of the organic phase, which is previously dried over sodium sulphate, there is obtained 4-*n*-pentylphenyl-malonic tetraacetal.

7.33 g of 4-*n*-pentylphenyl-malonic tetraacetal in 20 ml of ethanol are stirred overnight at 50°C under nitrogen with 0.72 ml of water and 2 drops of concentrated sulphuric acid. The acidic pentylphenyl-malonic aldehyde obtained as a by-product can be separated from the neutral 2-(4-*n*-pentylphenyl)-3-ethoxy-acrolein by extracting the mixture after dilution with ether, with aqueous sodium carbonate solution.

4.46 g of this 3-ethoxy-acrolein and 3.63 g of the foregoing 4-amidinobenzoic acid amide hydrochloride are stirred in a solution of 0.584 g of sodium metal in 250 ml of methanol overnight at room temperature under nitrogen. The yellow suspension is then filtered and the residue is washed with a small

amount of ethanol and suspended in 1.4 l of ether for further purification. The suspension is washed with water and then filtered again. Sparingly soluble 4-[5-(4-*n*-pentylphenyl)-2-pyrimidinyl]-benzoic acid amide is obtained.

4.2 g of 4-[5-(4-*n*-pentylphenyl)-2-pyrimidinyl]-benzoic acid amide are left under reflux for 1 h while stirring in a mixture of 200 ml of ethylene chloride and 2.5 ml of phosphorus oxychloride. The mixture is diluted with ether and washed with 2 N sodium hydroxide solution and then with water until neutral. After drying the organic phase over sodium sulphate and evaporation, there is obtained 5-(4-*n*-pentylphenyl)-2-(4-cyanophenyl)pyrimidine which is filtered through a short silica gel column and subsequently recrystallized from methylene chloride/methanol; m.p. 125°C ; clp. 241°C .

NMR δ 0.7–2.0 ppm (9, m), 2.67 (2, t, $J = 7.5$ Hz), 7.28, 7.53 (4, centers of AA'BB'-spectrum), 7.70, 8.57 (4, centers of AA'BB'-spectrum), 9.01 (2, s); mass spectrum m/e (%) 327 (M, 52), 270 (100), 115 (24), no other peak larger than 5%.

$\text{C}_{22}\text{H}_{21}\text{N}_3$

Calcd	C 80.70	H 6.46	N 12.83,
Found	C 80.77	N 6.28	N 12.80.

The corresponding 5-(4-*n*-alkoxyphenyl)-2-(4-cyanophenyl)pyrimidines are prepared in an analogous manner.

2-(4-*n*-Hexylphenyl)-5-(4-cyanophenyl)pyrimidine (3, R = C_6H_{13} , Scheme 3)

4.5 g of 4-bromophenyl-malonic tetraacetal, prepared in a similar manner as described in the synthesis of compounds 2, are dissolved in 10 ml of ethanol. The solution is treated with 0.5 ml of water and 1 drop of concentrated sulphuric acid and the mixture is stirred overnight at 50°C and then worked up in the customary manner.

2.5 g of this crude 2-(4-bromophenyl)-3-ethoxy-acrolein in 20 ml of methanol and then 2.4 g of 4-*n*-hexylbenzamidinium hydrochloride [2] are added

Scheme 3. Synthesis of 2-(4-hexylphenyl)-5-(4-cyanophenyl)pyrimidines.

to a sodium methylate solution obtained from 0.7 g of sodium in 25 ml of methanol. The mixture is heated to the reflux overnight. The solvent is then partially distilled off, the residue is treated with water and subsequently acidified with dilute hydrochloric acid. The resulting precipitate is filtered off, washed thoroughly with water and ether and dried. The crude 2-(4-*n*-hexylphenyl)-5-(4-bromophenyl)-pyrimidine of melting point 152.5–156 °C is used in the process without further purification.

1.9 g of 2-(4-*n*-hexylphenyl)-5-(4-bromophenyl)-pyrimidine in 50 ml of dimethylformamide are heated to reflux for 21 h with 2.5 g of copper(I) cyanide. After cooling, the mixture is stirred with 25 ml of 10% aqueous ethylenediamine solution and then extracted with methylene chloride. The extract is washed again with ethylenediamine solution and then several times with water until it gives a neutral reaction. The crude product obtained after evaporation is chromatographed on 150 g of silica gel with toluene/1% acetone. Initially there are obtained traces of the starting material and then fractions containing pure 2-(4-*n*-hexylphenyl)-5-(4-cyanophenyl)-pyrimidine. After recrystallization from ethyl acetate, the product has a melting point of 121.5 °C and a clearing point of 247.5 °C.

NMR δ 0.7–1.9 ppm (11, m), 2.70 (2, t, $J = 7$ Hz), 7.28, 8.35 (4, centers of AA'BB'-spectrum), 7.72 (4, nearly s), 8.93 (2, s); mass spectrum m/e (%) 341 (M, 52), 284(10), 274(38), 270(100), 127(9), no other peak larger than 5%.

C₂₃H₂₃N₃

Calcd	C 80.91	H 6.79	N 12.31,
Found	C 80.89	H 6.94	N 12.09.

5-*n*-Pentyl-2-(4'-cyano-4-biphenyl)-pyrimidine (4, R = C₅H₁₁, Scheme 4)

34.5 g of 4-bromobiphenyl in 164 ml of methylene chloride are treated at approx. 2 °C with 60.6 g of titanium tetrachloride. 20.7 g of dichloromethyl methyl ether are added dropwise at the same temperature over a period of 40 min. The cooling bath is then removed and the mixture is stirred for 21 h at room temperature. The mixture is poured on to ice and the product is extracted with ether in the customary manner. Chromatography on silica gel 60 with benzene as the eluting agent initially gives unreacted starting material and then 4'-bromo-4-biphenylaldehyde.

From 17.5 g of 4'-bromo-4-biphenylaldehyde and 4.4 g of hydroxylamine hydrochloride in 35 ml of methanol and 70 ml of pyridine there is obtained, after boiling under reflux, crude oxime which is converted into the nitrile by heating for 15 h in acetic anhydride. The mixture is concentrated as much as possible on a rotary evaporator. The residue is poured on to ice and dilute sodium hydroxide solution and the product is isolated with ether in the customary manner.

After treatment with hexane, the 4'-bromo-4-cyanobiphenyl melts at approx. 150 °C.

Scheme 4. Synthesis of 5-alkyl-2-(4'-cyano-4-biphenyl)-pyrimidines.

Dry hydrogen chloride is passed into a mixture of 5.6 g of 4'-bromo-4-cyanobiphenyl and 1 g of absolute ethanol in 25 ml of toluene until the mixture becomes saturated. After stirring for 3 days at room temperature, the precipitate is filtered off and washed with toluene. The residue is suspended in 5 ml of absolute ethanol whilst still moist and the suspension is treated with 1.3 g of ammonia in the form of a 10% ethanolic solution. After stirring for 3 days at room temperature, the precipitated 4'-bromo-4-biphenylamidine hydrochloride is separated, washed with ether and dried. 5.8 g of *n*-pentyl-malonic tetraacetal [7] in 10 ml of ethanol are stirred overnight at room temperature with 0.75 ml of water and 1 drop of concentrated sulphuric acid. The mixture is then diluted with ether, extracted with sodium carbonate solution, washed neutral and evaporated.

1.42 g of the thus-obtained crude 2-*n*-pentyl-3-ethoxy-acrolein [7] are dissolved in a sodium ethylate solution (obtained from 480 mg of sodium in 40 ml of ethanol) and 2.6 g of the 4'-bromo-4-biphenylamidine hydrochloride are added. The mixture is then stirred for 3 days at room temperature. After some of the solvent has been distilled off, water is added and the mixture is extracted with chloroform in the customary manner. Upon crystallization from ethanol, there is obtained 5-*n*-pentyl-2-(4'-bromo-4-biphenyl)-pyrimidine in the form of needles of melting point 137 °C and clearing point 197 °C.

1.5 g of 5-*n*-pentyl-2-(4'-bromo-4-biphenyl)-pyrimidine are heated to reflux for 22 h with 2.5 g

of copper(I) cyanide in 50 ml of dimethylformamide. After cooling, 25 ml of 10% aqueous ethylenediamine solution are added and, after stirring for a short time, the mixture is shaken again with 25 ml of ethylenediamine solution and then washed until it gives a neutral reaction. The crude concentrate is chromatographed on silica gel 60 with toluene/1% acetone. Recrystallization of the pure fractions from ethyl acetate yields 5-*n*-pentyl-2-(4'-cyano-4-biphenyl)-pyrimidine; m.p. 124 °C; clp. 259.5 °C.

NMR δ 0.92 ppm (3, nearly t, $J=7$ Hz), 1.25–1.8 (6, m), 2.65 (2, t, $J=7.5$ Hz), 7.68, 8.51 (4, centers of AA'BB'-spectrum), 7.72 (4, nearly s), 8.64 (2, s); mass spectrum m/e (%) 327 (M, 100), 270 (92), 243 (14), 204 (19), 177 (5), 39 (23), no other peak larger than 5%.

C₂₂H₂₁N₃

Calcd C 80.70 H 6.46 N 12.83,

Found C 80.49 H 6.46 N 12.77.

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