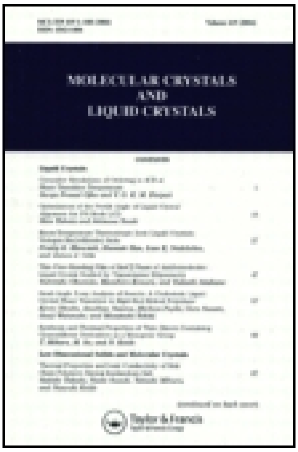

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Synthesis and Mesomorphic Properties of 2-N-Hexyl-6-(4-N-Alkoxybenzoyloxy) Quinoline

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Synthesis and Mesomorphic Properties of 2-*N*-Hexyl-6-(4-*N*-Alkoxybenzoyloxy) Quinoline

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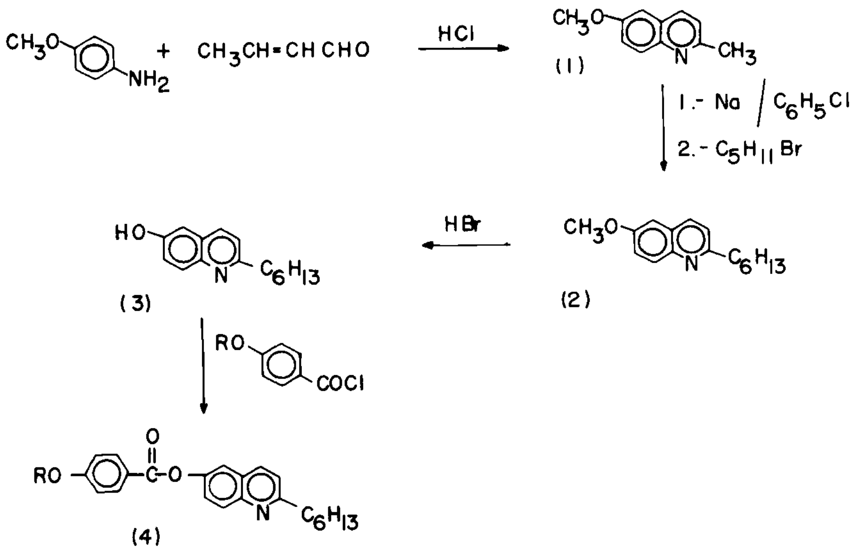
The synthesis and mesomorphic properties of the 2-*n*-hexyl-6-(4-*n*-alkoxybenzoyloxy) quinoline series are described for alkoxy chain lengths varying from three to nine carbon atoms. Generally the lower homologs show a nematic and a smectic phase and the higher homologs only a smectic phase. X-ray and optical measurements indicate that the smectic phase can be classified as a probable smectic A phase. The transition temperatures are similar to those of the corresponding derivatives of naphthalene.

INTRODUCTION

That naphthalene compounds can show mesomorphic behavior is well known and in recent years a number of new mesomorphic naphthalene compounds[1-5] have been reported. However, only a few quinoline compounds have been reported[6,7] even though the corresponding quinoline and naphthalene compounds are isogeometric.

We report the synthesis and mesomorphic properties of the 2-*n*-hexyl-6-(4-*n*-alkoxybenzolyloxy) quinoline series which is isogeometric with the 2-*n*-alkyl-6-alkoxybenzoyloxy) naphthalene series reported by Coates and Gray.[1] The incorporation of a hetroatom in the naphthalene ring should in principle increase the polarizability and the lateral component of the permanent electric dipole moment. Therefore, one should expect a change in the mesomorphic properties with the introduction of the hetroatom.

The 2-*n*-hexyl-6-(4-*n*-alkoxybenzolyloxy) quinolines (4) were synthesized according to Scheme I. The compound (1) was obtained by condensation between crotonaldehyde and aniline in 6N HCl. The product was recovered from the reaction mixture by the addition of an equimolar amount of zinc chloride,[8] which caused precipitation of 6-methoxyquinaldine hydrochloride-ZnCl complex. The free 6-methoxyquinaldine (1) was recovered in a yield of 52%, from the complex by



SCHEME I

treatment with ammonium hydroxide. Phenylsodium was used in the synthesis of compound (2) and the best result was obtained when the sodium was melted (105°C) and dispersed in toluene by vigorous mechanical stirring and later external cooling.

The 6-methoxyquinaldine sodium compound was alkylated with *n*-pentylbromide. Cleavage of the ether (2) with hydrogen bromide gave 2-*n*-hexyl-6-quinolinol (3) which when treated with 4-*n*-alkoxybenzoic acid chlorides gave the corresponding esters (4).

The structures for all these compounds were confirmed by IR (Perkin-Elmer 237 and 577), ^{1}H NMR (Varian T-60A), and ^{13}C NMR (Varian CFT-20), using Tetramethyl silane as the standard and elemental analysis (Table II).

RESULTS AND DISCUSSION

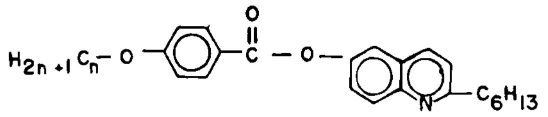
Transition temperatures and enthalpies were determined using a Perkin-Elmer DSC-2 calibrated with Indium. The transition temperatures were checked and textures observed using a Leitz Ortholux polarizing microscope with a Mettler FP-52 heated stage.

The transition temperatures and enthalpies are given in Table I and graphs of the variation in transition temperature and enthalpy as a function of the number of carbon atoms (n) in the alkoxy chain are shown in Figures 1 and 2. For $n = 3$, there exists only a monotropic nematic phase and for $n = 4$ and 5 there is an enantiotropic nematic phase and a monotropic smectic phase. For $n = 6$ both the nematic and smectic phases are enantiotropic. For $n > 6$, the nematic phase is absent and there remains only the enantiotropic smectic phase.

The texture observed with the polarizing microscope for the smectic phase was

TABLE I

a) Transition temperatures (°C); b) the enthalpies (kJ/mol) of the series



Compd.	R	F	SA		N		I
(4a)	$n\text{-}C_3H_7$	a) 83.1 b) 33.6	-	-	-	(79.7)	-
(4b)	$n\text{-}C_4H_9$	a) 78.1 b) 32.8	-	(65.8)	-	95.0 1.35	-
(4c)	$n\text{-}C_5H_{11}$	a) 79.1 b) 31.0	-	(71.9)	-	89.4 0.87	-
(4d)	$n\text{-}C_6H_{13}$	a) 80.9 b) 29.1	-	90.8 2.53	-	94.9 1.82	-
(4e)	$n\text{-}C_7H_{15}$	a) 84.9 b) 32.5	-	94.0 5.23	-	-	-
(4f)	$n\text{-}C_8H_{17}$	a) 78.5 b) 29.3	-	98.8 5.8	-	-	-
(4g)	$n\text{-}C_9H_{19}$	a) 84.1 b) 33.3	-	99.2 5.92	-	-	-

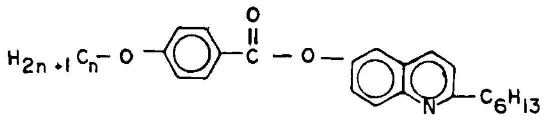
the focal-conic or the homeotropic texture. The homeotropic texture observed in convergent light shows a centered uniaxial positive cross.

X-ray diffraction patterns were recorded using a flat plate camera with the sample in 0.7 mm Lindemann capillaries in a temperature controlled oven. The diffraction pattern, for example, of compound (4d) in the smectic phase at 85°C showed one diffuse external ring and one sharp inner ring whose angular positions were constant as a function of temperature. The inner ring, using Bragg's Law, corresponds to a layer thickness of 28.2 ± 2.0 Å. The molecular length calculated for the fully extended molecule is 29.6 Å. The X-ray and convergent light data show that the smectic phase is of the orthogonal type without order within the smectic layers and thus we can classify the phase as a smectic A.

Preliminary measurements of dielectric anistropy give $\Lambda\varepsilon = \varepsilon_N - \varepsilon_1 = -0.5$. The negative dielectric anistropy can be attributed to the hetroatom in the ring system.

TABLE II

Elemental analysis of quinoline derivatives (4)



Compd.	R	Empirical formula	C Found (Calc.)	H Found (Calc.)
(4a)	n-C_3H_7	$C_{25}H_{29}NO_3$	76.85 (76.73)	7.22 (7.42)
(4b)	n-C_4H_9	$C_{26}H_{31}NO_3$	77.28 (77.04)	7.90 (7.65)
(4c)	n-C_5H_{11}	$C_{27}H_{33}NO_3$	77.13 (77.33)	8.14 (7.87)
(4d)	n-C_6H_{11}	$C_{28}H_{35}NO_3$	77.62 (77.60)	8.53 (8.04)
(4e)	n-C_7H_{15}	$C_{29}H_{37}NO_3$	78.02 (77.85)	8.63 (8.29)
(4f)	n-C_8H_{17}	$C_{30}H_{39}NO_3$	78.32 (78.09)	8.79 (8.46)
(4g)	n-C_9H_{19}	$C_{31}H_{41}NO_3$	78.42 (78.32)	8.95 (8.63)

The transition temperatures and phases for the two homologs of 2-*n*-alkyl-6-(4-*n*-alkoxybenzoyloxy) naphthalene reported by Coates and Gray[1] are very similar to those of the quinoline derivatives of this work. Both the naphthalene and quinoline derivatives have melting points on the order of 80°C and relatively short temperature range nematic and smectic A phases.

However, the transition temperature to the isotropic phase is higher for the naphthalene derivatives by about 20 to 30°C.

It is apparent that the presence of the hetroatom in the ring does not increase the polarizability of the molecule and if anything reduces it. The increase in lateral dipole moment also apparently does not lead to higher thermal stability for the smectic phase. We conclude that the results for the naphthalene and quinoline derivatives are similar because they are the same molecule from a geometric viewpoint.

EXPERIMENTAL

Preparation of 2 methyl-6-methoxyquinoline (1)

(1) was prepared according to Leir[8]
Yield 52% b.P$_{0.5}$ 118°C. ^{1}H-NMR δH. (CDCl$_3$) 2.2 (3H, s, CH$_3$); 3.2 (3H, s, OCH$_3$); 6.4 (1H, *d*, ^2j 3Hz); 6.6 (1H, *d*, ^1j 9Hz); 6.9 (1H, *d* of *d*, ^1j 9Hz, 2*j*, 3Hz); 7.2 (1H, *d*, *j* 9Hz); 7.6 (1H, *d*, ^1j 9Hz).

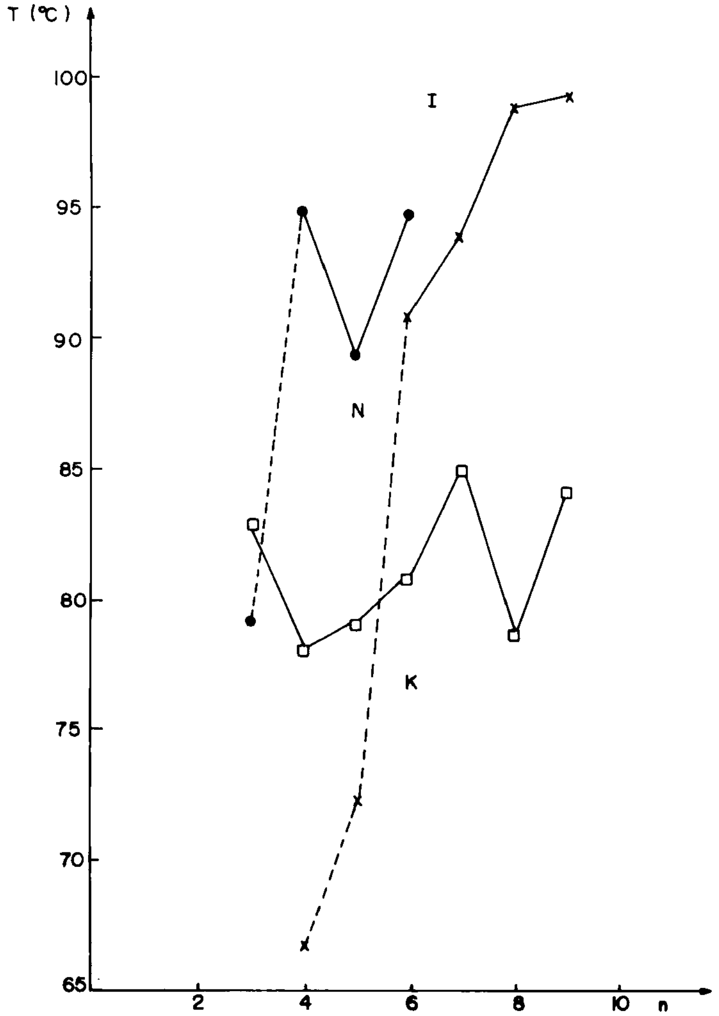


FIGURE 1 Phase transition temperatures as a function of the number of carbon atoms (*n*) in the alkoxy chain for the series 2-*n*-hexyl-6-(4-*n*-alkoxybenzoyloxy) quinoline.

Preparation of 2-*n*-hexyl-6-methoxyquinoline (2)

Compound (2) was obtained from 2-methyl-6-methoxyquinoline (1) by metallation with phenylsodium in analogy to the procedure reported for the preparation of 2-*n*-butylquinoline.[9]

The 6-methoxy quinaldinesodium compound was alkylated with *n*-pentylbromide; the organic phase was washed with water, dried (Na_2SO_4) and the solvent removed. The residue was vacuum destillated. Fraction 1 solidifies at r.t. and corresponds to the starting compound (1), fraction 2 was a mixture and fraction 3, a yellow liquid corresponding to compound (2) with a yield of 58%. An analytical sample was prepared by redestillation of fraction 3.

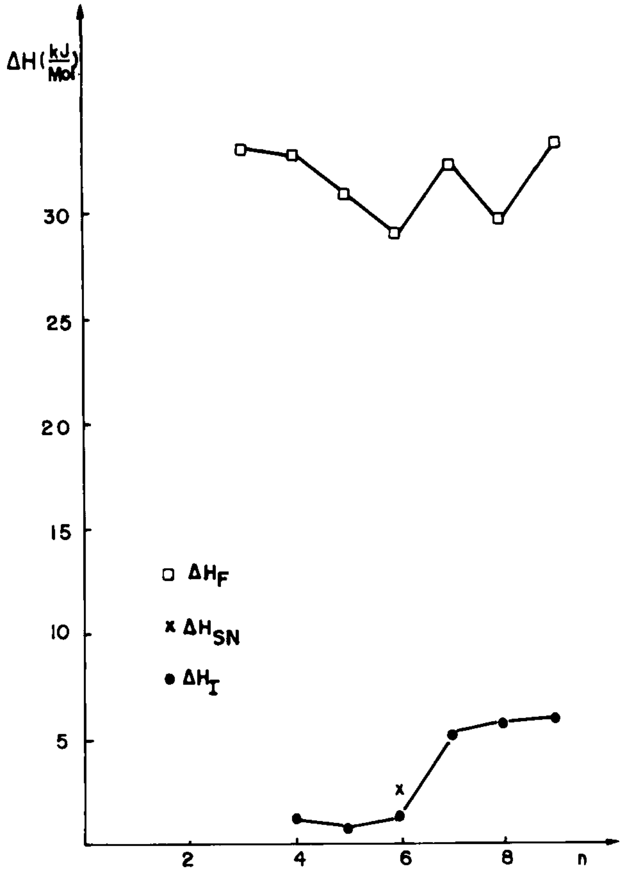


FIGURE 2 Transition enthalpies as a function of the number of carbon atoms (*n*) in the alkoxy chain for the series 2-*n*-hexyl-6-(4-*n*-alkoxybenzoyloxy) quinoline.

b.p.$_{0.25}$ 156°C; 78. 69 (Calc. 79.00); H, 9.06 (Calc. 8.64) IR (KBr) (cm^{-1}) 1600 (C=C) and 1230 (C—O) ^{1}H-NMR δ_H ($CDCl_3$) 0.3–1.8 (11H, *m*, C_5H_{11}); 2.5 (2H, *t*, CH_2); 3.2 (3H, *s*, OCH_3); 6.4–7.9 (5H, *m*, ArH) ^{13}C-NMR δC ($CDCl_3$) 160.04; 157.00; 143.91; 130.14; 127.41; 121.53; 121.28; 121.28; 104.96 (Ar.C) and 54.96; 38.85; 31.63; 29.78; 29.16; 22.51; 13.93 (Aliph. C).

Preparation of 2-*n*-hexyl-6-hydroxyquinoline (3)

The procedure reported for 6-hydroxyquinoline was used.[10]

To 2-methyl-6-methoxyquinoline (10) (0.005 mol) was added an equimolar quantity of sulfuric acid. The salt which separated from the solution and 37% HBr (50 ml) were refluxed for 12 hr. The dark mixture was poured into ice water, exactly neutralized with ammonia, extracted with methylene chloride and the organic layer washed with water, dried and evaporated. The crude sirupy product was used without further purification. Recrystallization from CCl_4 was possible only in small quantities. m.p. 105.9°C.

C, 78.35 (calc. 78.60); H, 8.68 (calc. 8.29) IR(KBr) (cm^{-1}) 3450 (O—H weak broad band) and 1600 (C=C); ^{1}H-NMR δH ($CDCl_3$) 0.6–2.1 (11H, *m*, C_5H_{11}); 3.3 (2H, *t*, CH_2); 7.2–8.6 (5H, *m*, ArH); 10.8 (1H, *s*, OH). ^{13}C-NMR- δC (C_6D_6) 158.69; 155.59; 141.73; 135.94; 128.43; 126.39; 122.57; 121.50; 109.42 (Ar.C) and 38.02; 31.54; 30.20; 29.02; 22.40; 13.9 (Aliph. C).

Preparation of 2-*n*-hexyl-6-(4-*n*-alkoxybenzoyloxy)quinoline (4)

4-Alkoxybenzoic (0.011 mol) and thionyl chloride (20 ml) were refluxed for 2 h. Excess thionyl chloride was removed under vacuum. A solution of 2-*n*-hexyl-6-hydroxyquinoline (3) (0.019 mol) in benzene (20 ml) was added in small portions to a stirred mixture of the acid chloride in benzene (20 ml) and pyridine (1 ml) refluxed for 2 hr and then poured into water (100 ml). The precipitate collected, was washed with water, dried and recrystallized from methanol. Yield 38% (the acid chloride and compound (3) were used without purification).
2-*n*-Hexyl-6-(4-*n*-octyloxybenzoyloxy) quinoline (4f)
IR(KBr) (cm^{-1}) 1720 (C=O) and 1600 (C=C)
^{13}C-NMR, δC (C_6D_6) 164.76; 164.00; 162.64; 148.97; 146.81; 135.59; 132.67; 131.07; 127.28; 125.04; 122.38; 121.99; 118.81; 114.78, (C=O and Ar.C), and 68.39; 39.32; 21.18; 29.70; 26.32; 23.07; 14.38 (Aliph. C).

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