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Synthesis and mesomorphic properties of 6-*n*-decyloxy-2-[4′-*N*-alkoxyphenylimino)methyl]quinolines (IV)†

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The synthesis and mesomorphic properties of a new series of liquid crystals derived from quinoline with an imine central bond is described. All compounds exhibit mesophase ranges greater than 50°C. The lower homologues ($n=4$–6) show trimorphism S_C–S_A–N (for $n=4$, the S_C phase is monotropic). The higher homologues ($n=7$–10) show nematic and smectic C phases. Compared to the styrylquinoline analogues the imine bond gives rise to similar liquid crystal phase ranges but lower melting points.

1. Introduction

In the last years, heterocyclic liquid crystals have been of great scientific interest. The presence of heterocycles as a part of the core provide perpendicular dipolar moments as well as polarizable structures, which can lead to S_C phases. Likewise the fact that the symmetry of the molecule is reduced results in lower melting points, and low temperature mesophases are promoted.

Among the different heterocyclic central cores those containing the quinoline ring have rarely been studied [1–6], rather less than the liquid crystalline behaviour of the homocyclic analogue, the naphthalene system, for which new possibilities have being realised [7–9].

Continuing our work on the liquid crystal possibilities of the quinoline system, we describe in this paper the synthesis and the mesogenic properties of a series of Schiff's bases derived from 2,6-disubstituted-quinolines.

2. Synthesis

The route used for the synthesis of this series of compounds is shown in the scheme.

Compounds **II** were obtained by the condensation of the crotonaldehyde and 4-*n*-alkoxyanilines (**I**) in 6 M HCl. The products were extracted from the reaction mixture by the addition of an equimolar amount of zinc chloride [10] which caused the precipitation of 6-*n*-alkoxy-2-methylquinoline hydrochloride–ZnCl complex. The free quinoline derivatives (**II**) were obtained in a 50 per cent yield from the complex by the treatment with ammonium hydroxide.

Aldehydes **III** were synthesized by the oxidation of **II** with freshly prepared and sublimated selenium dioxide [11, 12]. In the synthesis of compound **IIIa**, ethanol was used as the solvent [13], because it did not form the bisulphitic aduct, and its purification was carried out by vacuum distillation. The yield was low (30 per cent).

For the preparation of the aldehyde **IIIb**, using toluene as solvent [14] a better yield was obtained (80 per cent).

The Schiff's base series **IV** was obtained by the condensation of the aldehyde **III** with the corresponding 4-*n*-alkoxyaniline **I**.

3. Results and discussion

3.1. *Transitional behaviour*

Transition temperatures and enthalpies are given in table 1, and in figure 1, the phase transition temperatures are plotted against the number of carbon atoms *n* in the terminal alkyl chain of the phenyl ring.

All the homologues exhibit nematic mesophases. The nematic–isotropic phase transition temperatures show a slight odd–even alternation as the aliphatic chain length increases. From $n=6$ onwards the melting points increase with increasing chain length.

The first members of the series ($n=4$–6) exhibit trimorphism S_C–S_A–N (the S_C phase is monotropic for $n=4$). The higher homologues ($n=7$–10) exhibit only S_C and N mesophases.

In order to show the different possibilities that the quinoline ring can offer in the liquid crystal field, it is

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†In memory of Professor Juan Bartulín Fodic.

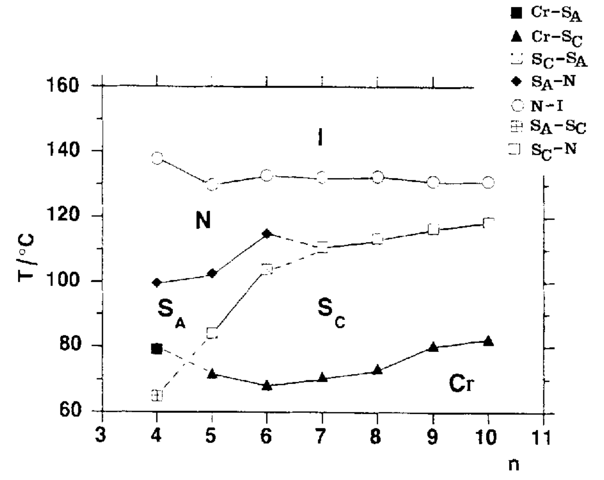
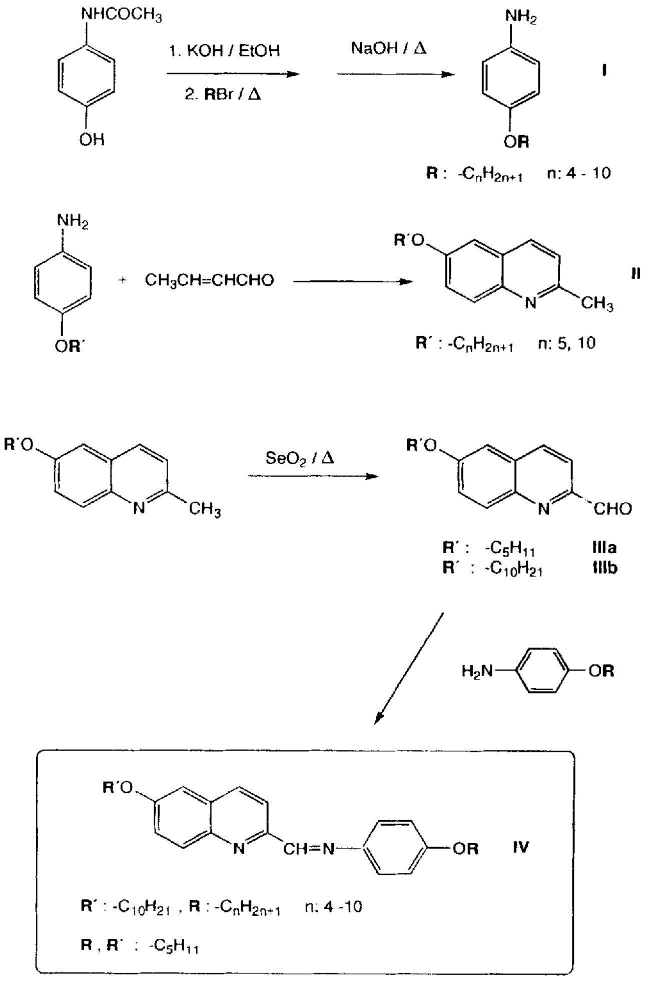


Figure 1. Plot of transition temperatures versus the number of carbon atoms (n) in the alkyl chain C_nH_{2n+1} of the Schiff's bases.



Scheme.

interesting to compare the mesogenic properties of this series of Schiff's bases with the series of styrylquinoline analogues previously synthesized and reported by us [3].

Table 2 and figure 2 show the mesogenic properties of these 6-*n*-pentyloxy-2-(4-*n*-alkoxystyryl)quinolines.

In both series the length of the chains attached to the quinoline ring differs (for the Schiff's bases, $R = n\text{-}C_{10}H_{21}$, styrylquinolines $R = n\text{-}C_5H_{11}$), except in the Schiff's base where $R = n\text{-}C_5H_{11}$ and $n = 5$.

However, some significant differences between both central cores can be noted as would be expected; the longer the molecular length the lower melting point, for the imine series. However, on the contrary the styryl central core stabilizes the liquid crystalline order (around 30°C). Both central linkages give rise to similar mesophase temperature ranges, see table 3.

It is also possible a comparison between the Schiff's base with $n = 5$ and the styrylquinoline with $n = 10$; these homologues are similar in length, see table 4.

Even though the terminal chains differ in length, in this case, the two molecules similar in length exhibit comparable trends to those reported for the whole series.

On the other hand, a noticeable influence of both central cores on the mesogenic order can be observed. Both promote nematic and smectic C phases, but an intermediate smectic A phase is observed for the shorter Schiff's bases while a highly ordered crystal G phase was detected for the longest members of the styryl series. This phase was not observed for the imine homologues despite their greater molecular length. The carbon–carbon double bond gives rise to a more planar structure [15] than the imine linkage [16] allowing for stronger molecular interactions in both the solid and the liquid crystalline phases which could explain the higher melting and clearing temperatures of the styryl-derivatives.

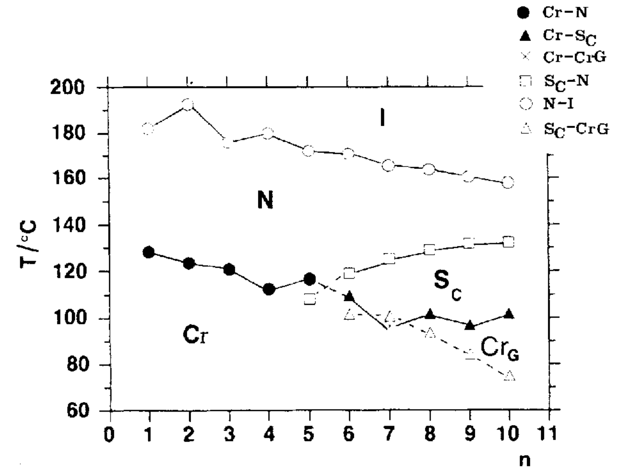
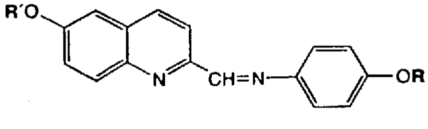


Figure 2. Plot of transition temperatures versus the number of carbon atoms (n) in the alkyl chain (R) of the styrylquinolines.

Table 1. Transition temperatures and enthalpies data of the Schiff's bases.



R'	R: $-C_nH_{2n+1}$	Transition	T/°C	ΔH/kJ mol^{-1}
n-$C_{10}H_{21}$	$n=4$	Cr–S_A	79·1	34·37
		S_A–N	99·7	0·19
		N–I	137·9	1·48
		S_A–S_C	65^a	
	$n=5$	Cr–S_C	71·9	27·95
		S_C–S_A	84^a	
		S_A–N	102·7	0·10
		N–I	129·9	1·29
	$n=6$	Cr–S_C	68·4	42·09
		S_C–S_A	104^a	
		S_A–N	115^a	
		N–I	132·8	1·90
	$n=7$	Cr–S_C	71·0	69·9
		S_C–N	109·9	0·19
		N–I	132·3	1·72
	$n=8$	Cr–S_C	73·4	50·10
		S_C–N	113·4	0·13
		N–I	132·5	1·77
	$n=9$	Cr–S_C	80·4	61·38
		S_C–N	116·6	0·20
		N–I	131·1	1·84
	$n=10$	Cr–S_C	82·4	60·54
		S_C–N	118·7	0·332
		N–I	131·1	2·75
n-C_5H_{11}	$n=5$	Cr–S_A	99·4	36·02
		S_A–N	124·6	0·83
		N–I	141·4	0·86

[a] Optical microscopy data.

3.2. *Characterization of the Schiff's bases*

The identity of the mesophases exhibited by these compounds has been assigned on the basis of their optical textures and confirmed by X-ray diffraction studies.

The nematic phase showed the typical schlieren texture with characteristic two- and four-brush singularities. On cooling this phase, its colour gradually changed to finally adopt a homeotropic texture before passing into the S_A or S_C phase. The tendency of these compounds to give rise to homeotropic alignment is noteworthy. The orthogonal S_A phase was characterized by a homeotropic texture coexisting with focal-conic fans. The S_C mesophase was identified by the appearance of a schilieren texture on both heating and cooling, showing a strong change of colour with temperature as the tilt angle varied (see figure 3).

3.3. *X-ray study*

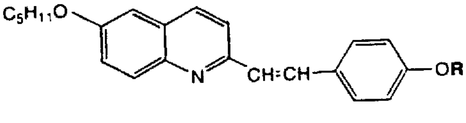
The mesophases were also characterized by X-ray diffraction at several temperatures. The S_A and S_C phases were confirmed by the presence of a sharp peak at low angles and the absence of any Bragg peak. From the scattering angle of this reflection, the Bragg equation gives rise the layer spacing. For the compounds with either the sequence N–S_C or N–S_A–S_C, a decrease in the smectic C layer spacing with a decrease in temperature was observed. A comparison between the layer spacing in the S_A phase and the molecular length of the molecules in a fully extended conformation (estimated from Dreiding stereomodels) showed the measured lengths to be around 6 Å shorter than the estimated layer spacings. From these data, intermolecular distances of 4·5–4 Å were also determined.

4. Experimental

4.1. *Analysis*

The purity of the compounds was evaluated by thin layer chromatography and elemental analysis (see table 5). The IR spectra were recorded using KBr discs (spectrophotometer Perkin–Elmer 577). ^{1}H and

Table 2. Transition temperatures and enthalpies data of the 6-*n*-pentyloxy-2-[4-*n*-alkoxystyryl]quinolines.



$R = -C_nH_{2n+1}$	Transition	Temperature/°C	ΔH/kJ mol^{-1}
$n = 1$	Cr–Cr	81·4	1·19
	Cr–N	128·4	30·65
	N–I	182·2	0·56
$n = 2$	Cr–Cr	101·6	11·75
	Cr–N	123·5	28·84
	N–I	192·7	0·54
$n = 3$	Cr–N	120·7	30·71
	N–I	176·1	0·65
$n = 4$	Cr–N	112·5	25·33
	N–I	180·1	0·83
$n = 5$	Cr–Cr	93·9	8·64
	Cr–N	116·6	18·10
	N–I	172·1	0·47
	(N–S_C)	(108·1)	−1·88
$n = 6$	Cr–S_C	109·8	21·74
	S_C–N	119·1	12·00
	N–I	170·9	0·88
	(S_C–CrG)	(101·7)	−6·42
$n = 7$	Cr–Cr	94·3	
	Cr–CrG	96·4	32·08
	CrG–S_C	100·7	
	S_C–N	125·2	2·18
	N–I	165·4	0·88
	(S_C–CrG)	(99·3)	−5·20
$n = 8$	Cr–Cr	92·86	7·15
	Cr–S_C	101·78	21·45
	S_C–N	129·2	1·99
	N–I	163·7	0·98
	(S_C–CrG)	(93·7)	−4·44
$n = 9$	Cr–S_C	97·0	39·83
	S_C–N	131·9	2·07
	N–I	160·5	1·00
	(S_C–CrG)	(86·4)	−4·09
$n = 10$	Cr–Cr	94·43	19·56
	Cr–S_C	101·81	22·22
	S_C–N	132·4	1·60
	N–I	157·9	1·05
	(S_C–CrG)	(75·08)	—

Parentheses denote a monotropic transition.

^{13}C NMR were recorded on a 250 Hz Bruker Ac-250p spectrometer (see table 6).

The textures of the mesophases were studied with an Olympus BH-2 polarizing microscope, using clean glass substrates, equipped with a Mettler FP82 hot stage. Transition temperatures were determined by differential scanning calorimetry using a Perkin–Elmer DSC 7 calorimeter with a heating and cooling rate of 5°C min^{-1}. The apparatus was calibrated with indium at 5°C min^{-1} (156·6°C, 28·45 J g^{-1}).

Powder X-ray diffraction patterns were obtained in a Gunier diffractometer (Huber 644) operating with CuK$_{\alpha_1}$ beam issued from a germanium monochromator. The samples were held in rotating Lindermann glass capillaries (diameter 0·5 mm) and heated with a variable temperature attachment. The diffraction patterns were registered with a scintillation counter.

4.2. *Synthesis*

4-n-Alkoxyanilines (**I**) were synthesized according to [17].

2-Methyl-6-n-alkoxyquinolines (**II**) were prepared using

Table 3. Comparison of the transition behaviour between the Schiff's base and stryrylquinoline linkages, both with pentyl terminal chains.

Transition	Transition temperature/°C
Schiff's base ($R = R' = n$–C_5H_{11})	
Cr–S_A	99·4
S_A–N	124·6
N–I	141·4
Styrylquinoline ($R = R' = n$–C_5H_{11})	
Cr–Cr	93·9
Cr–N	116·6
N–I	172·1
N–S_C	(108·1)

Parentheses denote a monotropic transition.

Table 4. Comparison of the transition behaviour between the Schiff's base and stryrylquinoline linkages, where $n=5$ and 10, respectively.

Transition	Transition temperature/°C
Schiff's base ($n=5$)	
Cr–S_C	71·9
S_C–S_A	84·0
S_A–N	102·7
N–I	129·9
Styrylquinoline ($n=10$)	
Cr–Cr	93·9
Cr–N	116·6
N–I	172·1
N–S_C	(108·1)

Parentheses denote a monotropic transition.

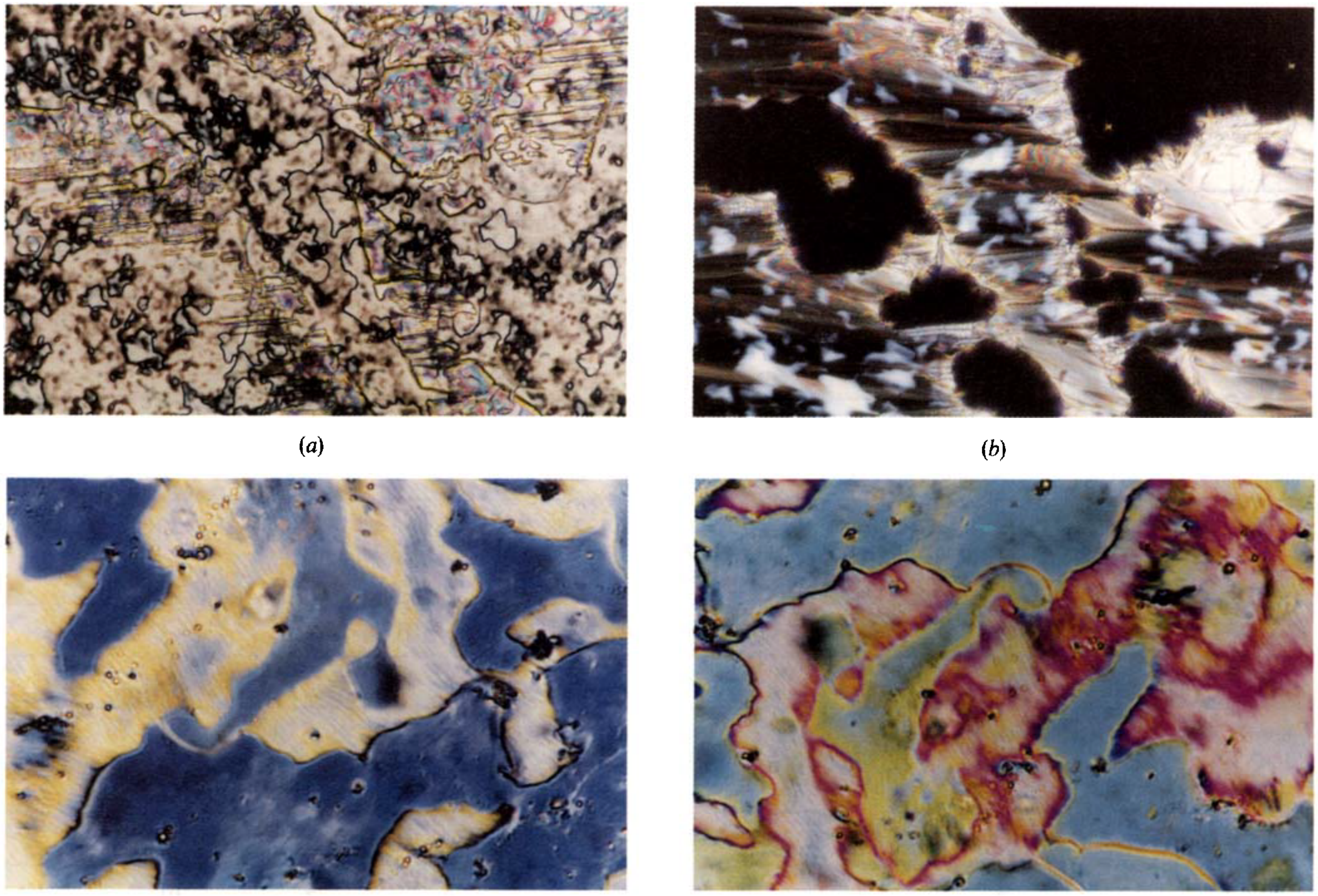
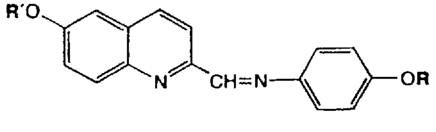


Figure 3. (*a*) Nematic schlieren texture of compound **IV** ($n=4$) at 107·9°C (× 66). (*b*) Variant of a focal-conic texture (S_A) of compound **IV** ($n=4$) at 90·7°C. (*c*) Schlieren texture with blue zone (S_C) at 95°C of compound **IV** ($n=6$), and change in colour when the analyser is turned at 70°C (*d*).

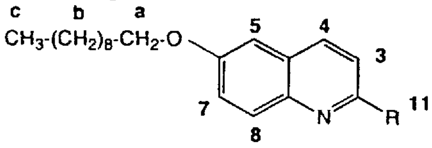
Table 5. Elemental analysis of 6-*n*-decyloxy-2-[(4′-*N*-alkoxyphenylimino)methyl]quinolines (**IV**).



R':-$C_{10}H_{21}$, R:-C_nH_{2n+1} n:4–10

			C		H	
R'	R: $-C_nH_{2n+1}$	Empirical formula	Calculated	Found	Calculated	Found
n-$C_{10}H_{21}$	$n=4$	$C_{30}H_{40}N_2O_2$	78·26	78·39	8·69	9·26
	$n=5$	$C_{31}H_{42}N_2O_2$	78·48	78·01	8·86	9·15
	$n=6$	$C_{32}H_{44}N_2O_2$	78·69	78·45	9·02	8·97
	$n=7$	$C_{33}H_{46}N_2O_2$	78·88	79·37	9·16	9·52
	$n=8$	$C_{34}H_{48}N_2O_2$	79·07	78·75	9·30	9·58
	$n=9$	$C_{35}H_{50}N_2O_2$	79·24	79·23	9·43	9·84
	$n=10$	$C_{36}H_{52}N_2O_2$	79·41	79·86	9·56	9·60
n-C_5H_{11}	$n=5$	$C_{26}H_{32}N_2O_2$	77·23	76·99	7·92	7·68

Table 6. ^1H NMR and ^{13}C NMR spectral data and IR for the compounds **II**, **III**, **IV** ($n=7$).



Chemical shifts of ^1H NMR($CDCl_3$)-$R=CH_3$ (**II**)

3	4	5	7	8	11	a	b	c
7·23 (d) $J=8·7$	7·93(d) $J=8·1$	7·03(d) $J=2·7$	7·33(d, d) $J_{78}=9·1$ $J_{75}=2·7$	7·90(d) $J=8·4$	2·70(s)	4·06(t) $J=6·6$	1·25–1·95 (m)	0·88(t) $J=6·7$

Chemical shifts of ^{13}C NMR($CDCl_3$)-$R=CH_3$ (**II**)

2	3	4	5	6	7	8	9	10	11
156·71	122·75	135·51	106·59	157·3	122·68	127·96	144·46	130·56	25·61

Decyl group = 68·87, 32·51, 30·19, 30·18, 29·93, 29·84, 26·71, 23·28, 14·70

IR (cm^{-1}) = ν 1595 (C = C), 1215 (C–O)

Chemical shifts of ^1H NMR ($CDCl_3$)-$R=CHO$ (**III**)

3	4	5	7	8	11	a	b	c
7·80(d) *J*8·5	7·92(d) *J*8·5	6·90(d) *J*2·7	7·28(d, d) $J_{78}=9·3$ $J_{75}=2·7$	7·94(d) *J*9·2	10·01(d)	3·29(t) *J*6·5	1–1·75 (m)	0·75(t) *J*6·3

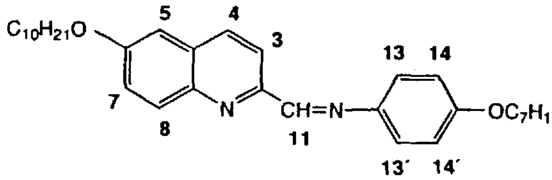
Chemical shifts of ^{13}C NMR($CDCl_3$)-$R=CHO$ (**III**)

2	3	4	5	6	7	8	9	10	11
150·84	118·02	135·75	105·90	159·83	124·17	132·17	144·21	131·96	193·69

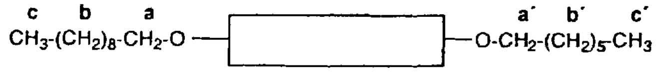
Decyl group = 68·89, 32·32, 30·00, 29·82, 29·75, 29·49, 26·47, 23·10, 14·52

IR (cm^{-1}) = ν 1690 (C = O), 1605 (C = O), 1210 (C–O)

Table 6. (*continued*)



Chemical shifts of ^{1}H NMR ($CDCl_3$)							
3	4	5	7	8	11	13–13′	14–14′
8·08 $J = 8{\cdot}79$	8·28(d) $J = 8{\cdot}78$	7·08(d) $J_{57} = 2{\cdot}92$	7·39(d, d) $J_{78} = 8{\cdot}79$ $J_{75} = 2{\cdot}93$	8·01(d) $J_{87} = 8{\cdot}97$	8·75(s)	7·35(d) $J = 9{\cdot}5$	6·93(s) $J = 9{\cdot}5$



a	a′	b + b′	c	c′
4·08(t)	3·97(t)	1·20–1·90(m)	0·88(t)	0·86(t)

Chemical shifts of ^{13}C NMR($CDCl_3$)													
2	3	4	5	6	7	8	9	10	11	12	13–13′	14–14′	15
153·22	135·68	119·53	106·65	159·24	123·46	131·64	144·57	143·48	158·98	130·69	123·39	115·67	158·85

Alkyl groups = 69·05, 68·92, 32·54, 32·43, 30·21, 30·04, 29·96, 29·80, 29·72, 26·72, 22·66, 23·31, 23·25

IR (cm^{-1}) = ν 1610 (C = N), 1222 (C–O)

the same method described in [10] for 6-methoxy-2-methylquinoline. The compound with $R = n\text{-}C_5H_{11}$ was purified by distillation, b.p. 0·04 122°C, m.p. 53°C. Elemental analysis (found C, 78·77; H, 8·47; $C_{15}H_{19}NO$ calculated C, 78·60; H, 8·30 per cent). The compound with $R = n\text{-}C_{10}H_{21}$ was purified by chromatography on silica gel using hexane/ethyl acetate (8:2) as eluent. The solids were recrystallized from *n*-hexane, cooling the solution to 0°C, m.p. 55°C. The yields were in the range of 45–50 per cent. Elemental analysis (found C, 80·60; H, 9·9; $C_{20}H_{29}NO$ calculated C, 80·26; H, 9·70 per cent).

6-n-Decyloxy-2-formylquinoline (**III**) was prepared according to the method described for the preparation of 6-methoxy-2-formylquinoline in [14].

29·9 g (0·1 mol) of 6-*n*-decyloxy-2-methylquinoline (**II**) were dissolved in 250 ml of toluene and the solution was stirred and heated to reflux. Sublimed selenium dioxide was added in two portions at 30 and 60 min. The mixture was then gently refluxed for 6 h. The black selenium was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was purified on silica gel using hexane/ethyl acetate (9·5:0·5) as eluent. m.p. 57°C. 80 per cent yield. Elemental analysis (found C, 76·43; H, 8·32; $C_{20}H_{27}NO_2$ calculated C, 76·68; H, 8·63 per cent).

6-n-Decyloxy-2-[(4-n-alkoxyphenylimino)methyl]-quinoline (**IV**) A solution of 5 mmol of 4-*n*-alkoxyanilinine in 20 ml of ethanol was added to a solution of 1·56 g (5 mmol) of 6-*n*-decyloxy-2-formylquinoline in 40 ml of ethanol. The mixture was stirred and heated for 30 min. The precipitate was filtered off and purified by chromatography on silica gel using hexane/ethyl acetate (8:2) as eluent, and then recrystallized from ethanol. Yield 85 per cent.

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