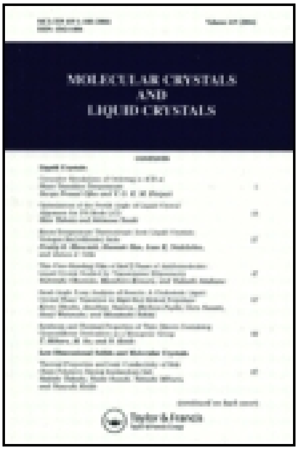

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Properties of the Liquid Crystals Formed by Certain Azomethines Derived from 4-Cycloalkylanilines and from 4-Cycloalkylbenzaldehydes

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Properties of the Liquid Crystals Formed by Certain Azomethines Derived from 4-Cycloalkylanilines and from 4-Cycloalkylbenzaldehydes†

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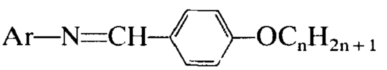
The liquid crystal behaviour of four homologous series of azomethines related to the nO.m series but containing a cycloalkyl group, is reported and discussed. Many of these compounds show extensive smectic polymorphism, one member of the nO.c6 series giving rise to five smectic polymorphic modifications for which phase type assignments have been made by thermal optical microscopy.

Keywords: smectic polymorphism, azomethines, cycloalkyl derivatives

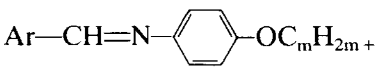
†Presented at the 11th International Liquid Crystal Conference, University of California, Berkeley, California, 30th June–4th July, 1986.

INTRODUCTION

The liquid crystal behaviour is reported of members of the series of N-(4-*n*-alkoxybenzylidene)-4′-cycloalkylanilines (1) derived from 4-cyclopentyl- and -cyclohexyl-aniline, and the 'reversed' series, the 4-*n*-alkoxy-N-(4′-cycloalkylbenzylidene)anilines (2), derived from 4-cyclopentyl- and -cyclohexylbenzaldehyde. These azomethines are related to the nO.m series[1] [of which the compound (3), MBBA or 1O.4 is a simple member].



(1)



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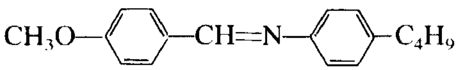
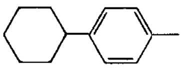
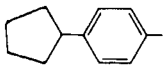


(3) MBBA, 1O.4

where Ar =  and Ar = 

By analogy with the nO.m nomenclature, the cycloalkyl substituted azomethines (1) are conveniently described as members of the nO.cm series and those of 'reversed' type (2) belong to cn.Om series.

Initially, our interest was only with series (1): Ar = 4-cyclohexylphenyl, the intention being to compare the known effect[2] of Ar = 4-biphenylyl with its 'half-reduced' Ar analogue. However, study of a range of homologues (n = 1–10, 12, 14, 16) of this nO.c6 series revealed very extensive smectic polymorphism reminiscent of the corresponding smectogenic nO.6 series. One member (n = 12) of the nO.c6 series gives rise to a nematic phase and five smectic polymorphic modifications for which phase type assignments have been made based on the textures observed by thermal optical microscopy. Related homologues, (1): Ar = cyclopentylphenyl (nO.c5) and those of the 'reversed' series (2): Ar = 4-cyclohexylphenyl (c6.Om) and Ar = 4-cyclopentylphenyl (c5.Om) show similar, though less pronounced smectic polymorphism.

RESULTS AND DISCUSSION

Transition temperatures for eleven or twelve [(n, m = 1 (or 2) – 10, 12, 14] or thirteen (also n = 16) members of each of the four series,

TABLE I

Transition temperatures for nO.c6 series; (1): Ar = 4-cyclohexylphenyl

n	C–I(N, S_A)	N(S_A)–I	S_A(S_C, S_G)–N	S_C(S_B)–S_A	S_G(S_B)–S_C	S_F–S_B	S_G–S_F	N(S_G, S_F)–C
	C–I	N–I						N–C
1	107	(92.5)						74.5
2	139	(118.5)						114
3	107	(95)						94
4	118	(105.5)						85.5
	C–N							
5	88.5	96						75
			S_G–N					S_G–C
6	84.5	102	(73)					72.5
7	76	97.5	(71.5)					66
			S_C–N		S_G–S_C			
8	79.5	100	(75)		(71)			38
			S_A–N	S_C–S_A				
9	95.5	97.5	(83)	(78.5)	(69)			39
	C–S_A							
10	85.5	99	89.5	(79.5)	(68.5)			34
					S_B–S_C			
12	87	97.5	94.5	(76)	(70.5)	(70)	(67.5)	39
		S_A–I		S_B–S_A				
14	88	95.5		(72.5)		(65.5)	(63.5)	52.5
								S_F–C
16	87.5	94		(75)		(71)		56.5

( ) monotropic transition

TABLE II

Transition temperatures for nO.c5 series; (1): Ar = 4-cyclopentylphenyl

n	C–I(N, S_G, S_A)	N(S_A)–I	S_A(S_G)–N	S_G–S_A(S_B)	S_B–S_A	S_F–S_B	N(I, S_G, S_F)–C
	C–I	N–I					N–C
1	96	(84)					82
	C–N						
2	104.5	110					97
	C–I						I–C
3	107						101
	C–N						N–C
4	95	98					92
	C–S_G		S_G–N				S_G–C
5	69.5	88	79				<25
6	78	94.5	84				<25
7	57.5	90.5	79				<25
8	60	94	81				<25
			S_A–N	S_G–S_A			
9	63	91.5	82.5	75.5			31
10	61	93	88	75.5			33
				S_G–S_B			
12	73.5	92	91.5	73.5	76.5		43
		S_A–I					
14	76	91.5		(68.5)	77.5		53.5
	C–S_A						S_F–C
16	84	90			(79.5)	(70)	68

( ) monotropic transition

TABLE III

Transition temperatures for c5.Om series; (2): Ar = cyclopentylphenyl

m	C–I(N, S_G)	N–I	S_G(S_A)–N	N(S_G, S_A)–C
	C–I			N–C
1	93	(87.5)		68
	C–N		S_G–N	S_G–C
2	107.5	113	(94.5)	80
	C–I			
3	94	(91)	(87)	78
	C–S_G			
4	80	102.5	89.5	75
	C–N			
5	83.5	93	84	58.5
6	89.5	98.5	(87)	77.5
7	85	93.5	(81.5)	67.5
8	88	95.5	(81.5)	76.5
9	86	92	(74.5)	74
10	86.5	93	(73.5)	73
				N–C
12	89.5	91		76
	C–I		S_A–I	S_A–C
14	91.5	88.5	(79)	78.5

( ) monotropic transition

(1) and (2): Ar = 4-cyclopentylphenyl and Ar = 4-cyclohexylphenyl, are listed in Tables I–IV and shown plotted against the number of carbon atoms (n,m) in the alkyl chain of the alkoxy group in Figures 1–4.

The results show clear similarities between the liquid crystal behaviour of the nO.5 and nO.6 series and their cycloalkyl analogues, the nO.c5 and nO.c6 series. The presence of the cycloalkyl group does, however, shift the onset of this behaviour to longer alkoxy chain lengths, and many of the smectic phases are monotropic as m.p.s. are higher in the nO.c5 and nO.c6 series. Comparison of the average values of $T_{N\text{-}I}$ for n = 4–7 shows that the nematic thermal stabilities of the nO.6 and nO.5 series are lower than those of their cycloalkyl analogues, nO.c6 and nO.c5, by 22.9°C and 10.2°C, respectively.

There are no data on n.Om series for comparison with the c5.Om and c6.Om series. However, for these cycloalkyl analogues, reversal of the azomethine linkage results in a similar pattern of behaviour except that smectic polymorphism is less extensive with its onset at higher homologues than in the nO.cm series. The compounds, in general, do not allow the same degree of supercooling as those of the nO.cm series.

TABLE IV

Transition temperatures for c6.Om series; (2): Ar = 4-cyclohexylphenyl

m	C–I(N)	N–I	$S_A(S_C, S_G)$–N	$S_A(S_G)$–S_C	I(N, S_C, S_G)–C
	C–N				N–C
2	116.5	120.5			86.5
	C–I				I–C
3	121				104
					N–C
4	117.5	(110.5)			101
5	104.5	(101.5)			95
	C–N				
6	92.5	106.5			80.5
			S_G–N		S_G–C
7	98.5	101	(75)		74
8	98.5	103	(77)		76
9	91	101	(72.5)		72
10	91.5	101	(73.5)		69
			S_C–N	S_G–S_C	
12	98.5	98.5	(76)	(67)	65
	C–I		S_A–N	S_C–S_A	S_C–C
14	97.5	95.5	(84)	(75.5)	74.5

( ) monotropic transition

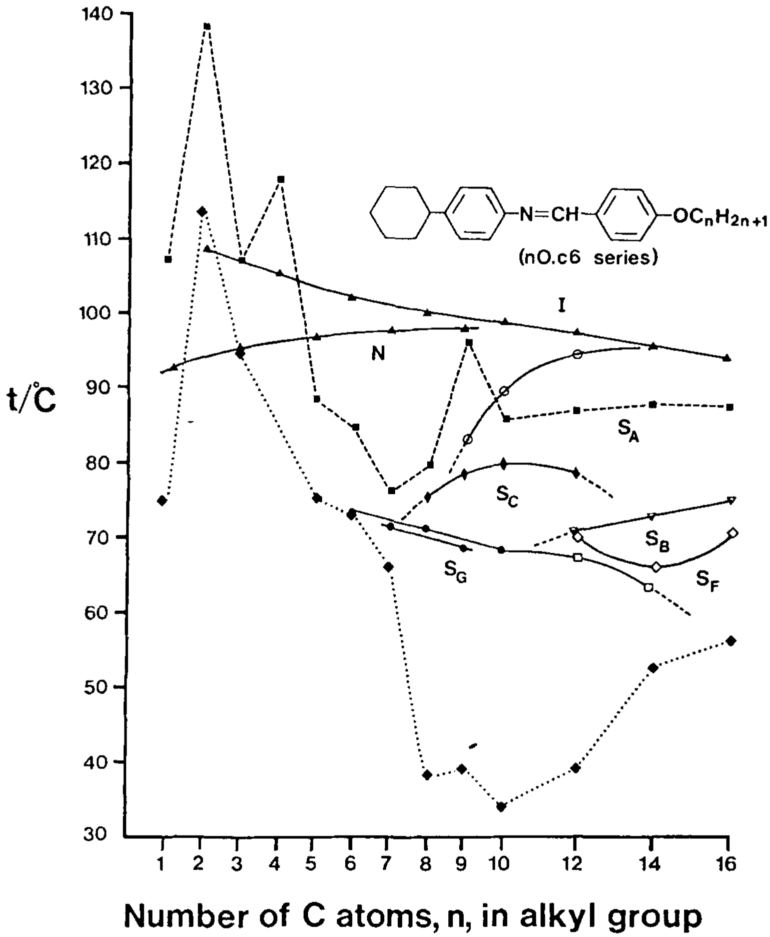


FIGURE 1 Plot of transition temperatures against the number of carbon atoms (n) in the alkyl chain of the N-(4-n-alkoxybenzylidene)-4′-cyclohexylanilines (nO.c6 series). ■---■---■ m.p.s., ♦---♦---♦, recrystallisation temperatures.

Optical textures

The various smectic polymorphic modifications were identified by thermal optical microscopy. Optical textures shown by the liquid crystal phases of the compound n = 12 of the nO.c6 series, N-(4-*n*-dodecylbenzylidene)-4′-cyclohexylaniline, are shown in the photomicrographs, Plates 1–6. The section of the sample is the same in each instance and contains a region in which orthogonal smectic phases

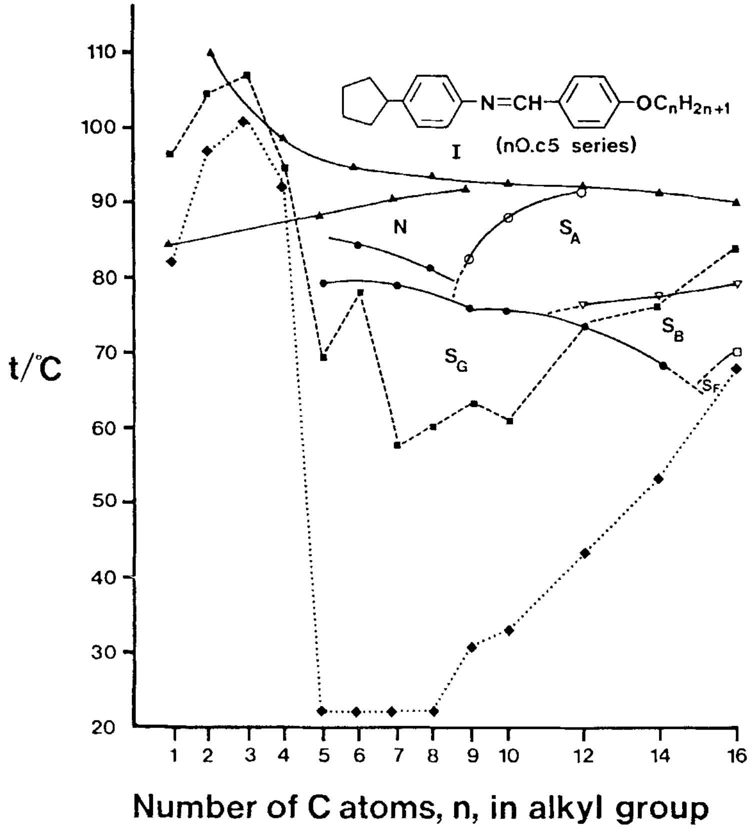


FIGURE 2 Plot of transition temperatures against the number of carbon atoms (n) in the alkyl chain of the N-(4-n-alkoxybenzylidene)-4′-cyclopentylanilines (nO.c5 series). ■---■---■ m.p.s., ♦---♦---♦, recrystallisation temperatures.

appear homeotropic. The smectic phase types assigned as S_A, S_C, S_B and S_G show textural characteristics which are typical of these phases as described in the texts by Gray and Goodby[3] and by Demus and Richter.[4] Similarly, the smectic phase that occurs intermediate between the S_B and S_G phases shows optical textures consistent with it being an S_F phase. At the transition to this phase on cooling the S_B phase, the previously smooth S_B fans become broken at their edges and then take on a mottled appearance with irregular birefringent colouring. Also the homeotropic region of the previous S_B phase is invaded, at first by a string-like interlocking network which lacks colour. This grows until the whole region is occupied by very small mosaic or *schlieren*-mosaic areas (rather than the *schlieren* texture

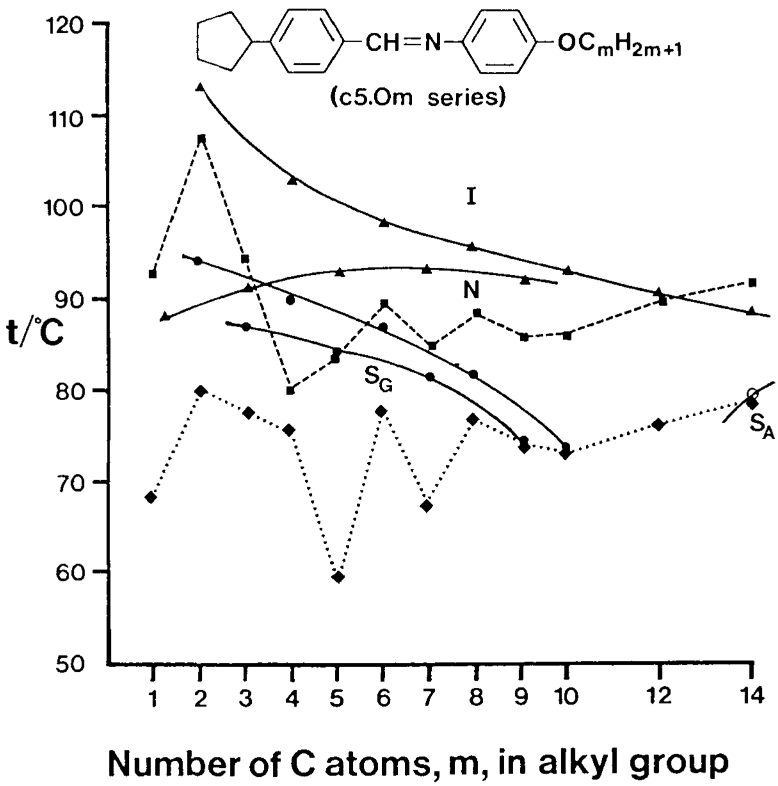


FIGURE 3 Plot of transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 4-n-alkoxy-N-(4'-cyclopentylbenzylidene)anilines (c5.Om series). ■---■---■ m.p.s., ♦---♦---♦, recrystallisation temperatures.

that might have been expected for an S_I phase). These textures are exactly analogous to those shown by the S_F phase of the compound 5O.6.[1] We consider, therefore, that the compounds 5O.6 and 12O.c6 show the same sequence of phases on cooling the isotropic liquid, namely I—N—S_A—S_C—S_B—S_F—S_G. Thus, as with the compound 5O.6 the S_F phase of the compound 12O.c6 occurs between the *more ordered* S_B and S_G phases.

The assignments of phase type by thermal optical microscopy will be confirmed by miscibility studies and by X-ray diffraction.

Characteristics of individual series

Some similar trends are apparent in all four series studied. Thus, as n(m) increases: (i) the onset of smectic properties is marked by the

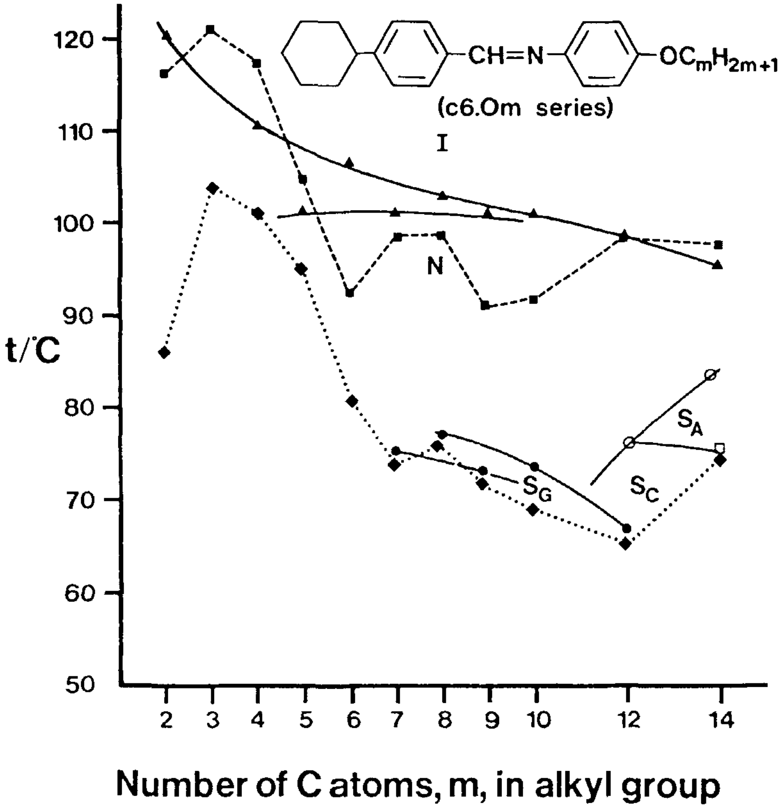


FIGURE 4 Plot of transition temperatures against the number of carbon atoms (m) in the alkyl chain of the 4-*n*-alkoxy-N-(4′-cyclohexylbenzylidene)anilines (c6.Om series). ■---■---■ m.p.s., ♦---♦---♦, recrystallisation temperatures.

occurrence of an S_G phase, (ii) S_G–N transition temperatures show odd-even (n,m) alternation, and (iii) N–I transition temperatures for even-n(m) members fall and those of odd-n(m) members initially rise.

nO.c6 series; (1): Ar = 4-cyclohexylphenyl (Figure 1, Table I). The early members are purely nematic. Smectic properties appear with an S_G phase at n = 6. At n = 8, on raising the temperature, the S_G phase gives rise to another tilted smectic, an S_C phase, before giving way to the nematic phase. For n = 9 and 10, there is similar behaviour except that an S_A phase is interposed between the S_C and the nematic phases. The S_G–S_C transition temperature curve rises to n = 10 then falls to n = 12, whereas the S_A–N transition temperatures continue to rise so that, for n = 14 and 16, S_A–N transitions replace the N–I transitions of earlier members.

PLATES 1–6. Photomicrographs of the optical textures shown by the liquid crystal phases of N-(4-*n*-dodecylbenzylidene)-4′-cyclohexylaniline (12O.c6) on cooling from the isotropic liquid. The section of the sample is the same in each instance and contains a region in which orthogonal smectic phases appear homeotropic.

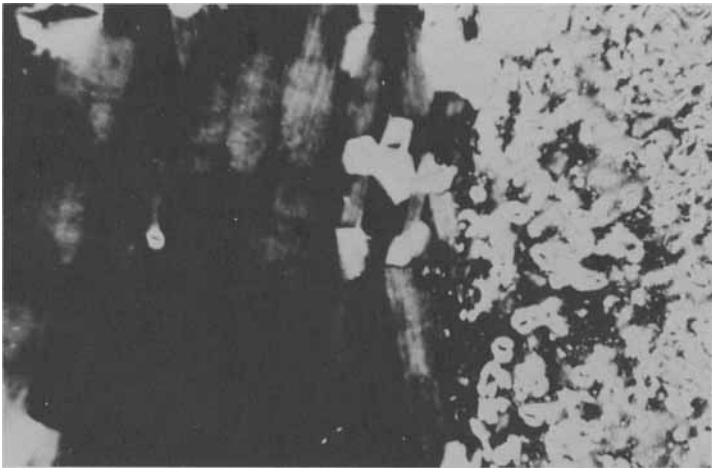


PLATE 1 Nematic phase. Schlieren texture on right hand side.

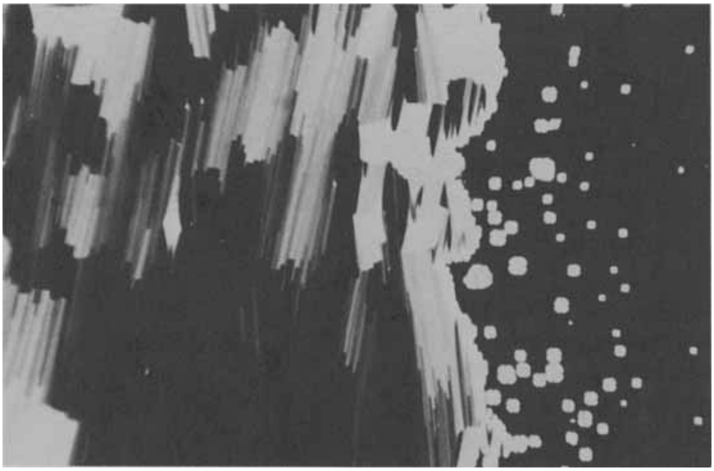


PLATE 2 Smectic A phase. Focal conic fan texture with a homeotropic region in the schlieren area of the previous nematic phase.

PLATE 3 Smectic C phase. Broken focal conic fan texture with a schlieren region in the homeotropic area of the previous S_A phase.

For n = 12, 14 and 16, the smectic polymorphism becomes rather complex. For n = 12, on raising the temperature, the S_G phase gives successively an S_F phase then an S_B phase (which persist for 2.5° and 0.5°C, respectively) before the S_C phase is formed, so that the sequence of phases is C, S_G, S_F, S_B, S_C, S_A, N, I. For n = 14 and 16, the S_C phase does not appear, and for n = 16, the onset of recrys-

PLATE 4 Smectic (crystal) B phase. The schlieren area of the previous S_C phase has become homeotropic. The transition bars at the S_C–S_B transition have left a number of 'fissures' in the fans. These slowly disappear on standing.

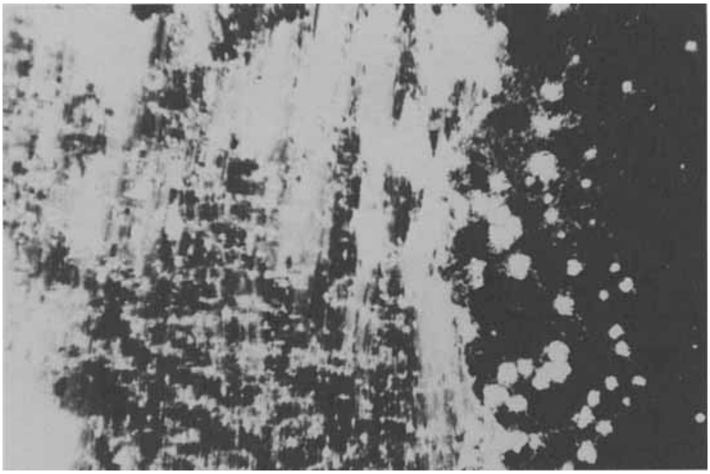


PLATE 5 Smectic F phase. The fans of the previous S_B phase have a broken, mottled appearance and a network of very small mosaic areas is developing in the homeotropic region of the previous S_B phase. This gradually fills the entire region.

tallisation obscures the formation of the S_G phase on cooling the S_F phase.

nO.c5 Series; (1): Ar = 4-cyclopentylphenyl (Figure 2, Table II). This series shows very similar trends to the nO.c6 series except that no S_C phases are evident. The early members are purely nematic. S_G phases appear at n = 5, and, as in the nO.c6 series, S_A phases

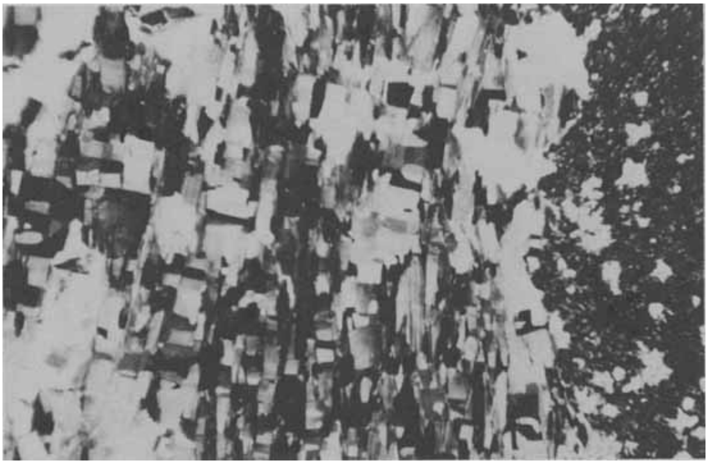


PLATE 6 Smectic G phase. Broken focal conic fan and mosaic textures. The fans have a characteristic patchwork or chequerboard appearance.

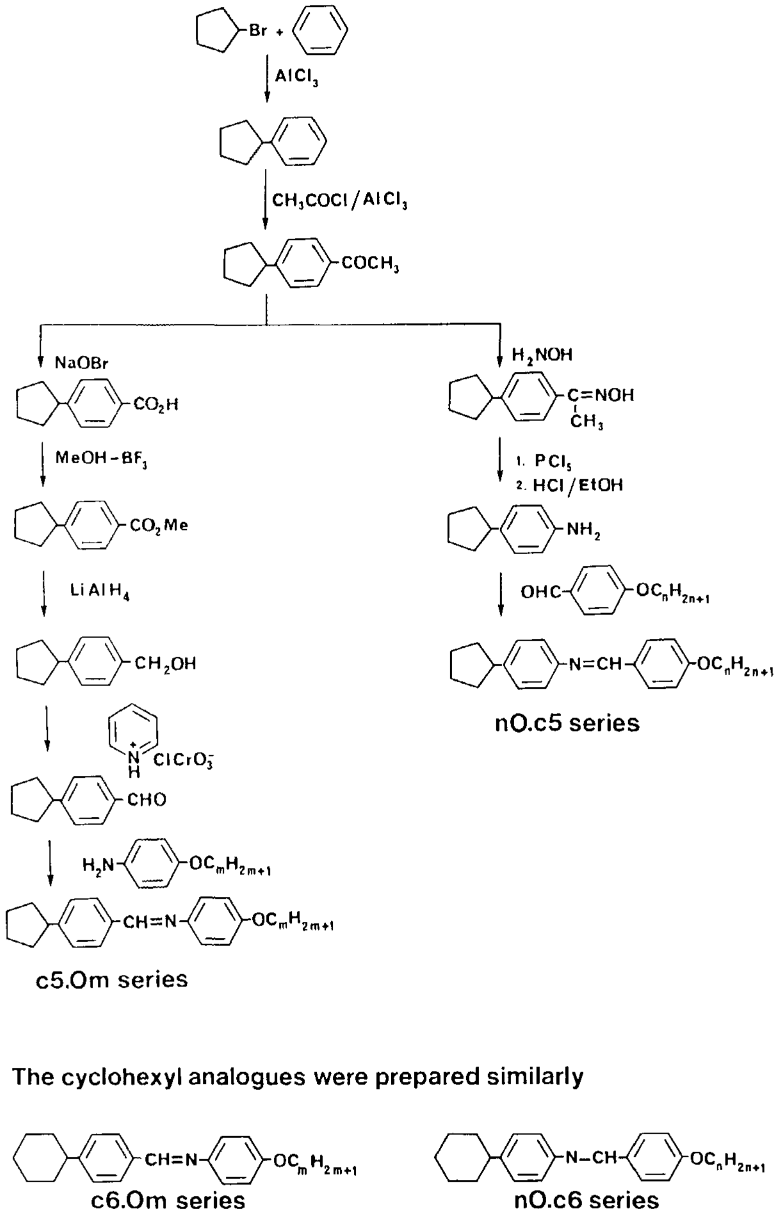


FIGURE 5 Synthetic scheme used for the preparation of the N-(4-*n*-alkoxybenzylidene)-4′-cycloalkylanilines (1) (nO.cm series) and the 4-*n*-alkoxy-N-(4′-cycloalkylbenzylidene)anilines (2) (cn.Om series).

occur at n = 9, the S_A–N transition temperatures lying on a rising curve that becomes coincident with the falling N–I curve at n = 14. For n = 12, 14 and 16, the S_A phase gives rise to an S_B phase on cooling so that for n = 12 and n = 14, S_G–S_B transitions occur, although for n = 16, the S_G phase is absent and there is an S_F–S_B transition instead.

c5.Om Series; (2): Ar = 4-cyclopentylphenyl (Figure 3, Table III). These compounds show nematic phases throughout (m = 1 to m = 14). S_G phases commence at n = 2 and the S_G–N transition temperature curves fall up to m = 10. For m = 9 and m = 10, recrystallisation occurs immediately after the N–S_G transition, and for the compound m = 12, recrystallisation extinguishes smectic properties. These reappear at m = 14 when an S_A–N transition occurs, presumably at the start of a curve rising to meet the N–I curve although higher members than n = 14 were not studied.

c6.Om Series; (2): Ar = 4-cyclohexylphenyl (Figure 4, Table IV). This series resembles the c5.Om series except that the early members have rather high recrystallisation temperatures which obscure the S_G phases so that S_G–N transitions do not appear until n = 7. In contrast with the c5.Om series, the compound n = 12 has a lower temperature of recrystallisation and shows both S_G and S_C phases. For n = 14, an S_A phase lies above the S_C phase, but the S_G phase does not occur.

Work on other cycloalkyl analogues is in progress.

EXPERIMENTAL

Materials

The azomethines were prepared by standard methods illustrated by the routes to the 4-cyclopentylphenyl derivatives, the 4-*n*-alkoxy-*n*-(4′-cyclopentylbenzylidene)anilines (c5.Om series) and N-(4-*n*-alkoxybenzylidene)-4′-cyclopentylanilines (nO.c5 series), shown in the synthetic scheme, Figure 5. Full experimental details of the synthetic work (which may be obtained on request to the authors, DJB or RCW) will appear in a future publication.

Physical measurements

Measurements of transition temperatures and microscope observations of textures of mesophases were made using a Vickers M75 polarising microscope in conjunction with a Mettler FP 52 hot-stage and FP 5 control unit.

Structural confirmation of the identity of intermediates (where necessary) and final products was obtained by standard techniques. I.r. spectra were recorded for KBr discs with a Perkin-Elmer 157 grating spectrophotometer, and ^{1}H n.m.r. spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as internal standard with a JEOL FX60Q Fourier transform spectrometer. Mass spectra were determined with an A.E.I. MS 902S spectrometer equipped with a Mass Spectrometry Services Analog Series 200 console and an INCOS 2300 data system.

Acknowledgements

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