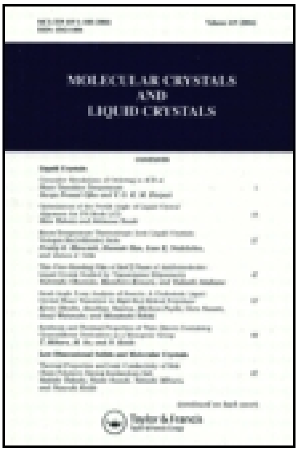


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Properties of the Liquid Crystals Formed by Certain Azomethines Containing Terminal Cycloalkyl Ring Systems

D. J. Byron [a], A. S. Matharu [a], M. Rees [a] & R. C. Wilson [a]
[a] Department of Chemistry and Physics, The Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS, England

To cite this article: D. J. Byron , A. S. Matharu , M. Rees & R. C. Wilson (1995): Properties of the Liquid Crystals Formed by Certain Azomethines Containing Terminal Cycloalkyl Ring Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 258:1, 217-228

To link to this article: http://dx.doi.org/10.1080/10587259508034562

Mol. Cryst. Liq. Cryst., 1995, Vol. 258, pp. 217–228
Reprints available directly form the publisher
Photocopying permitted by license only

Properties of the Liquid Crystals Formed by Certain Azomethines Containing Terminal Cycloalkyl Ring Systems

D. J. BYRON, A.S. MATHARU, M. REES and R. C. WILSON*

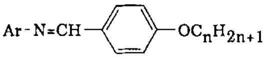
Department of Chemistry and Physics, The Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, England

(Received December 3, 1993)

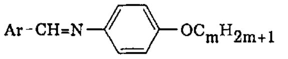
Fifty-six compounds containing cyclopropyl, cycloheptyl, or cyclooctyl ring systems, members of six homologous series of azomethines related to the nO.m series, have been prepared and their liquid crystal behavior investigated. These series show less extensive smectic polymorphism than the analogous cyclopentyl and cyclohexyl derivatives, previously reported. The effect on nematic thermal stability of an increase in the size of the cycloalkyl group present in related azomethines is discussed. Azomethines containing cyclopropyl, cycloheptyl and cyclooctyl rings have lower nematic thermal stability than their cyclopentyl and cyclohexyl homologues.

INTRODUCTION

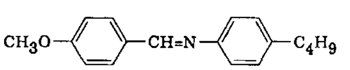
This paper completes an investigation of the liquid crystal behaviour of members of the series of *N*-(4-alkoxybenzylidene)-4′-cycloalkylanilines (1), 'reversed' series, the 4-alkoxy-*N*-(4′-cycloalkylbenzylidene)anilines (2).



(1) nO. cm

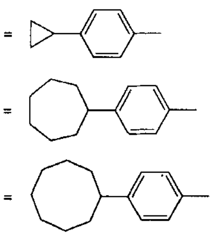


(2) cn. Om



(3) MBBA 1O. 4

where Ar =



These benzylideneanilines are related to the nO. m series [of which MBBA (3), 1O.4 is a simple member], and, by analogy, the *cyclo*alkyl substituted azomethines (1) and 'reversed' type (2), may be described as members of the nO.*c*m and *c*n.Om series, respectively.

Previous studies[1] of series (1) and (2) have shown that when Ar = 4-cyclopentylphenyl and Ar = 4-cyclohexylphenyl, quite extensive smectic polymorphism occurs

---

* Author for correspondence.

with clear similarities between the liquid crystal properties of the smectogenic nO.5 and nO.6 series and their cycloalkyl analogues, the nO.c5 and nO.c6 series. However, the presence of the cycloalkyl group shifts the onset of the occurrence of smectic behaviour to longer alkoxy chain lengths. For example, the compounds 5O.6 and 12O.c6 show the same sequence of phases, I-N-S_A-S_B-S_C-S_F-G on cooling the isotropic liquid.

Although the c5.Om and c6.Om series cannot be compared with the n.Om series due to lack of data, nevertheless in comparison with their 'reversed' nO.cm analogues they show rather less extensive smectic polymorphism, the onset of which is delayed to higher homologues.

Members of series (1) and (2), derived from the appropriate 4-cyclopropyl-, -cycloheptyl-, and -cyclooctyl-aniline or -benzaldehyde, have now been investigated in order to extend the study of the liquid crystal properties of these azomethines beyond the influence of 5- and 6-membered to 3-, 7-, and 8-membered alicyclic rings, i.e to both smaller and larger alicyclic systems.

RESULTS AND DISCUSSION

Transition temperatures for members of each of the six series, (1) and (2), Ar = 4-cyclopropylphenyl, Ar = 4-cycloheptylphenyl, and Ar = 4-cyclooctylphenyl are listed in Tables I–VI and shown plotted against the number of carbon atoms (*n*, *m*) in the alkyl chain of the alkoxy group in Figures 1–6. The series show interesting trends and some resemblances to their analogues with Ar = 4-cyclopentylphenyl and Ar = 4-cyclohexylphenyl, but do not reveal the extensive smectic properties of the *n*O.c5 and nO.c6 series. Different smectic modifications were identified from their optical textures when examined by thermal optical microscopy.

TABLE I

Transition temperatures[a] (°C) for the *N*-(4-alkoxybenzylidene)-4′-cycloheptylanilines (nO.c7 series)

n	C-I	C-N	C-S_A	N-I	G-N	S_A-N	S_C-S_A	G-S_C	I-C[b]	N-C[b]	S_C-C[b]	G-C[b]
1	95.6			(67.1)[c]						53.0		
2	125.5			(96.7)						87.0		
3	97.6			(71.9)*					73.5			
4	98.9			(85.4)						65.4		
5	83.2			(75.5)						61.0		
6	90.0			(83.9)						60.5		
7		62.2		79.4	(60.4)							25.0
8		70.3		83.5						62.6		
9		69.5		81.7		(63.5)	(63.1)				57.0	
10		76.8		83.7		(73.1)	(66.3)	(54.6)				52.5
12			77.6	84.6		80.5	(66.5)	(49.5)				48.0
14			81.6	82.8		82.1	(62.3)				62.3	

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic *A*, etc. Thus C-S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallization (at a cooling rate of approximately 4°C min^{-1}).

[c] Values in parentheses are for monotropic transitions.

* Transition temperature determined by observation of uncovered droplets

TABLE II

Transition temperatures (°C)[a] for the *N*-(4-alkoxybenzylidene)-4′-cyclooctylanilines (nO.c8 series)

n	C-I	C-N	N-I	S_A-N	S_C-N	S_A-S_C	I-C[b]	N-C[b]	S_C-C[b]
4	102.2		(59.1)*[c]				81.1		
5	90.7						55.7		
6	86.3		(61.0)					60.0	
7	65.6		(56.5)					44.4	
8	70.7		(62.9)		(43.4)*			46.0	
9	74.2		(60.9)		(45.5)*			50.0	
10	76.3		(64.9)	(53.9)		(51.0)			45.0
12		68.0	69.6	(66.1)		(55.2)			34.7

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic *A*, etc. Thus C-S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallization (at a cooling rate of approximately 4°C min^{-1}).

[c] Values in parentheses are for monotropic transitions.

* Transition temperature determined by observation of uncovered droplets.

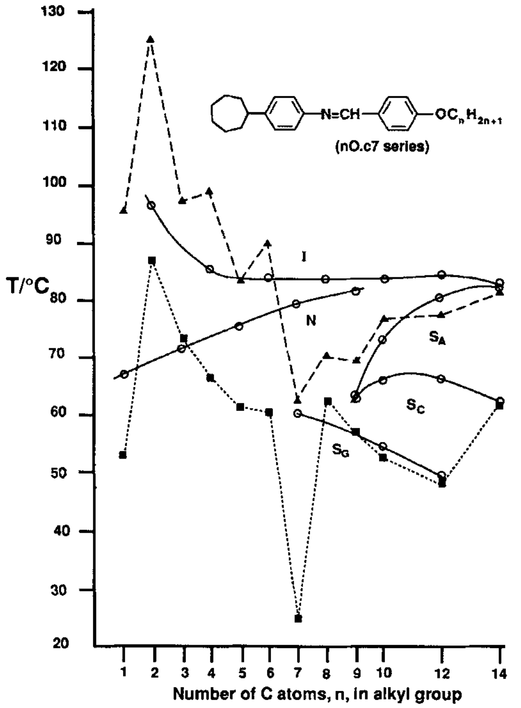


FIGURE 1 Plot of transition temperatures for *N*-(4-alkoxybenzylidene)-4′-cycloheptylanilines(nO.c7 series) ▲—▲ m.p.s; ■-----■ recrystallisation temperatures; ○—○ mesophase-mesophase or mesophase-isotropic liquid transition temperatures.

TABLE III

Transition temperatures[a] (°C) for the *N*-(4-alkoxybenzylidene)-4′-cyclopropylanilines (nO.c3 series)

n	C-I	N-I	S_A-I	G-I	S_A-N	G-N	S_A-S_B	G-C[b]	S_B-C[b]	I-C[b]
2	101.0									88.9
3	77.0			(58.4)[c]				52.0		
4	80.4									68.0
5	77.7	(57.8)				(57.0)		56.0		
6	77.4	(70.3)[c]				(64.7)		41.0		
7	81.5	(69.4)				(63.9)		63.7		
8	81.1	(75.3)				(70.3)		52.2		
9	85.3	(74.8)			(73.3)		(72.2)		60.2	
10	85.0	(77.2)			(77.0)		(74.1)		56.9	
12	88.0		(79.4)				(75.8)		66.1	

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic *A*, etc. Thus C-S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallization (at a cooling rate of approximately 4°C $\min^{-1}$).

[c] Values in parentheses are for monotropic transitions.

nO.c7 series; (1): Ar = 4-cycloheptylphenyl (Figure 1, Table I)

This series was the first to be studied in this investigation and twelve members ($n = 1$–10, 12, 14) were prepared. The general form of the transition temperature plot is very similar to that reported previously for the *n*O.c6 series but with lower T_{N-I} values.

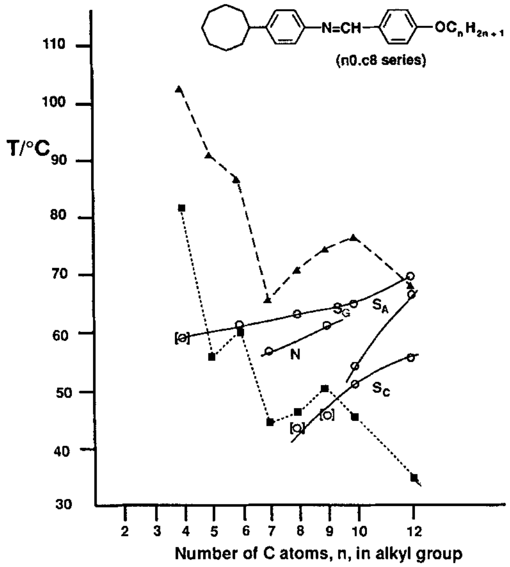


FIGURE 2 Plot of transition temperatures for *N*-(4-alkoxybenzylidene)-4′-cyclooctylanilines (nO.c8 series) ▲—▲ m.p.s; ■-----■ recrystallisation temperatures; ○—○ mesophase-mesophase or mesophase-isotropic liquid transition temperatures; [○] transition temperatures determined by observation of unconvered droplets.

TABLE IV

Transition temperatures[a] (°C) for the 4-alkoxy-*N*-(4′-cycloheptylbenzylidene)anilines (c7.Om series)

n	C-I	C-N	N-I	G-N	G-C[b]	N-C[b]
3	86.0		(72.5)[c]			66.4
4	96.9		(87.5)			66.4
5	79.2		(78.8)	(61.3)	60.0	
6		69.6	85.9	(69.2)	51.7	
7		68.3	81.6	(68.0)	25.0	
8		83.3	85.2	(68.5)	58.9	
9	83.2		(82.3)	(63.6)	62.6	
10		78.1	82.6	(60.3)	56.2	
12	88.1		(82.0)			60.4
14	87.8		(80.4)			59.3

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic *A*, etc. Thus C-S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallization (at a cooling rate of approximately 4°C min^{-1}).

[c] Values in parentheses are for monotropic transitions.

There is an alternation of the *N-I* transition temperatures, with the odd-*n* curve rising to meet the falling even-*n* curve. A crystal smectic *G* phase appears at $n = 7$ and continues with decreasing transition temperatures through to $n = 10$ and 12. The compounds $n = 9, 10, 12, 14$ show S_C and S_A phases. As *n* increases the S_A-*N* and S_C-S_A

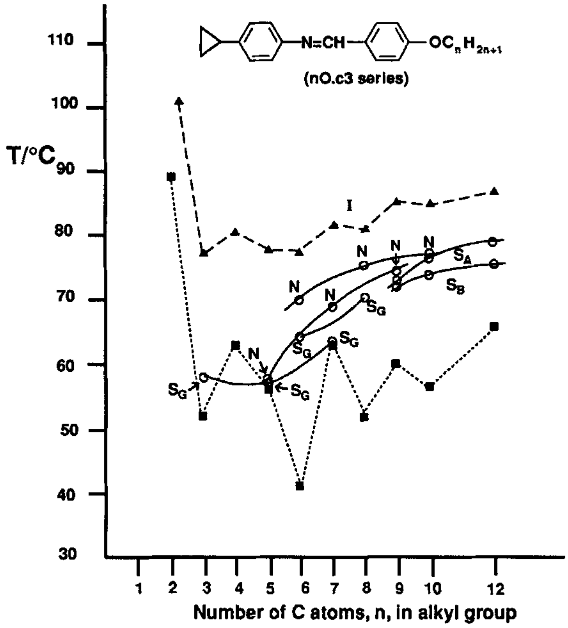


FIGURE 3 Plot of transition temperatures for *N*-(4-alkoxybenzylidene)-4′-cyclopropylanilines (nO.c3 series) ▲—▲ m.p.s; ■-----■ recrystallisation temperatures; ○—○ mesophase-mesophase or mesophase-isotropic liquid transition temperatures.

TABLE V

Transition temperatures[a] (°C) for the 4-alkoxy-*N*-(4-cyclooctylbenzylidene) anilines (c8.Om series)

n	C-I	N-I	N-G	N-C[b]	G-C[b]	I-C[b]
2	91.8	(65.8)*[c]				77.5
3	76.9	(37.7)		37.0		
4	83.7	(59.1)		58.3		
5	80.3	(50.2)	36.4	(36.0)		
6	78.0	(61.4)	(53.6)		50.0	
7	62.5	(56.6)	(51.7)		50.0	
8	72.1	(63.1)	(54.4)		45.0	
9	77.2	(59.4)		53.9		
10	77.7	(63.6)		48.0		
12	75.7	(64.8)		45.0		
14	81.3	(63.4)		63.0		

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic *A*, etc. Thus C-S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallization (at a cooling rate of approximately 4°C min^{-1}).

[c] Values in parentheses are for monotropic transitions.

* Transition temperature determined by observation of uncovered droplets.

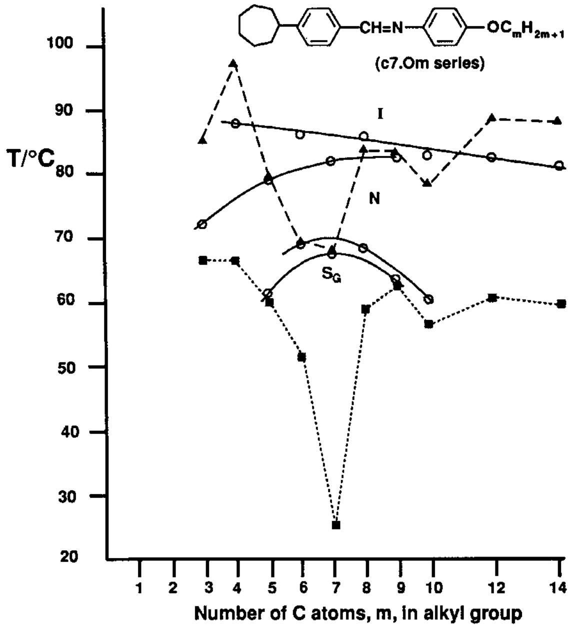


FIGURE 4 Plot of transition temperatures for 4-alkoxy-*N*-(4-cycloheptylbenzylidene)anilines(c7.Om series) ▲—▲ m.p.s; ■-----■ recrystallisation temperatures; ○—○ mesophase-mesophase or mesophase-isotropic liquid transition temperatures.

TABLE VI

Transition temperatures[a] (°C) for the 4-alkoxy-*N*-(4′-cyclopropylbenzylidene)anilnes (c3.Om series)

n	C-I	N-I	N-C[b]	I-C[b]
6	85.4	(68.8)*[c]		74.7
7	83.4	(65.0)*		78.6
8	84.8	(70.7)*		71.4
9	86.5	(68.1)*		74.1
10	85.2	(72.7)	72.4	

[a] Symbols have their usual meaning: C, crystal; I, isotropic liquid; N, nematic; S_A, smectic *A*, etc. Thus C-S_A represents the temperature (m.p.) at which a transition from the crystalline solid to the smectic A phase occurs.

[b] Temperature of crystallization (at a cooling rate of approximately 4°C min^{-1}).

[c] Values in parentheses are for monotropic transitions.

* Transition temperature determined by observation of uncovered droplets.

transition temperatures lie, respectively, on a continuously rising curve, and on a curve which at first rises and then falls. The S_B and S_F phases shown by the nO.c6 series are not formed.

nO.c8 series; (1): Ar = 4-cyclooctylphenyl (Figure 2, Table II)

Eight members (*n* = 4–10, 12,) of this series were prepared. The T_{N-I} values are lower than for the 4-cycloheptyl analogues and both odd- and even-n curves rise with

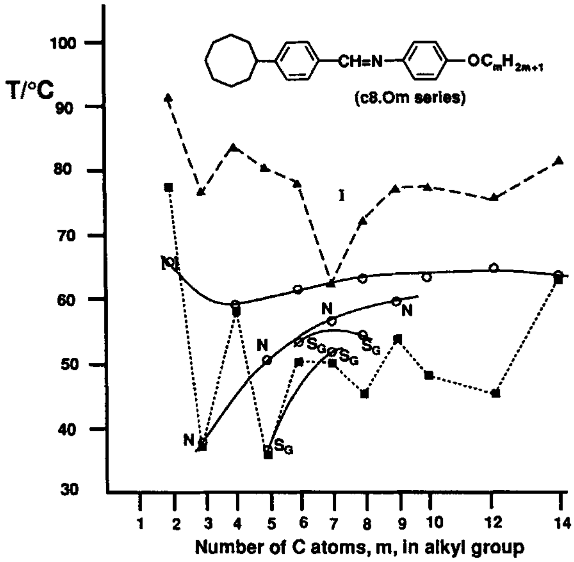


FIGURE 5 Plot of transition temperatures for 4-alkoxy-*N*-(4-cyclooctybenzylidene)anilines (c8.Om series) ▲—▲ m.p.s; ■-----■ recrystallisation temperatures; ○—○ mesophase-mesophase or mesophase-isotropic liquid transition temperatures; [○] transition temperature determined by observation of uncovered droplets.

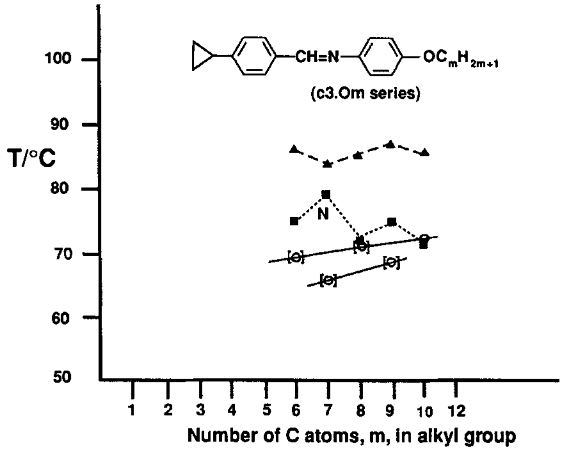


FIGURE 6 Plot of transition temperatures for 4-alkoxy-*N*-(4-cyclooctybenzylidene)anilines(c8.Om series) ▲––▲ m.p.s; ■-----■ recrystallisation temperatures; ○—○ mesophase-mesophase or mesophase-isotropic liquid transition temperatures; [○] transition temperatures determined by observation of uncovered droplets.

increasing values of *n*. Higher homologues give rise to S_A and S_C phases, but no *G* phases are formed.

nO.c3 series; (1): Ar = 4-cyclopropylphenyl (Figure 3, Table III)

Ten members ($n = 2$–10, 12) were investigated. Nematic properties are shown by the compounds $n = 5$–10, and the alternating *N*-*I* transition temperatures fit two curves which rise as *n* increases. Compounds $n = 3$–8 give rise to G phases, with an odd-even alternation in the same sense as the T_{N-I} values, whereas the compounds $n = 9$–12 form S_A then S_B phases on cooling from the isotropic liquid.

c7.Om series; (2): Ar = 4-cycloheptylphenyl (Figure 4, Table IV)

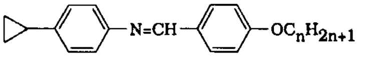
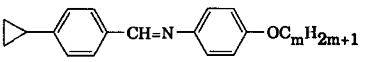
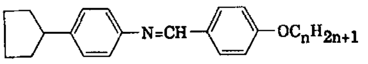
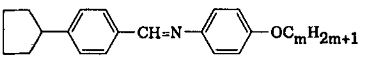
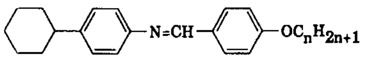
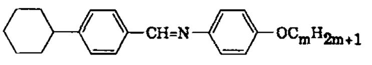
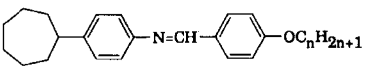
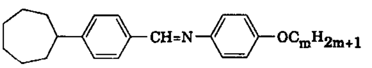
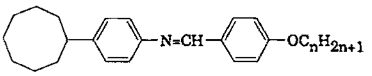
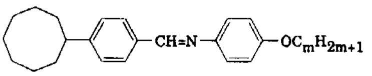
Ten homologues ($m = 3$–10, 12, 14) were studied. As with the 'reversed', nO.c7 series, falling even-*m* and rising odd-*m* *N*-*I* transition temperature curves are observed. No S_A nor S_C phases are formed, but the homologues $m = 5$–10 give rise to *G* phases, the *N*-*G* transition temperatures alternating in the same sense as the T_{N-I} values with the points lying on curves which rise to a maximum and then fall as *m* increases.

c8.Om series; (2): Ar = 4-cyclooctylphenyl (Figure 5, Table V)

Eleven members ($m = 2$–10, 12, 14) prepared. The plot of transition temperatures against *m* is very similar to that for the 4-cycloheptyl analogues, except that (i) the T_{N-I} values are lower and, both odd- and even-*m* curves rise with increasing *m* after $m = 2$, and (ii) the *G* phase is extinguished at $m = 8$ due to higher recrystallisation temperatures of the homologues $m = 9$ and 10.

TABLE VII

Azomethines of Type (1) (nO.cm) and Type (2) (cn.Om). Average *N-I* Transition Temperatures for *n*/*m* = 7–10.

Type	Azomethine	Average N–I (°C) (n/m = 7–10)	$\Delta T_{(1)-(2)}$
(1)		74.2	5.1
(2)		69.1	
(1)		92.3	− 1.2
(2)		93.5	
(1)		98.5	− 3.0
(2)		101.5	
(1)		82.1	− 0.8
(2)		82.9	
(1)		61.3	0.6
(2)		60.7	

c3.Om series; (2): Ar = 4-cyclopropylphenyl (Figure 6, Table VI)

Only five members (*m* = 6–10) of this series were studied, because, in contrast with the reversed nO.c3 series, this series of compounds only gives rise to monotropic nematic phases. The isotropic melts could not be extensively supercooled, and, with the exception of the compound *m* = 10, the transition temperatures were obtained by observation of individual small droplets of the sample on an uncovered microscope slide.

The results now available enable comparisons to be made of the effect on mesophase thermal stability of increasing the size of the cycloalkyl ring and of reversal of the azomethine linkage for members of five sets of the two series of benzylideneanilines, (1) and (2), for Ar = cyclopropyl-, -pentyl-, -hexyl-, -heptyl-, and -octyl-phenyl. Table VII summarises the average *N*-*I* transition temperatures of the heptyloxy-decyloxy homologues of each of the series investigated.

For each cycloalkyl group, reversal of the central linkage results in clear differences in the shapes of the plots (Figures 1 and 4, 2 and 5, 3 and 6 of this paper, and Figures 1 and 4; 2 and 3 of our earlier publication[1]) of transition temperature against *n* or *m*, the number of carbon atoms in the alkyl chain of the alkoxy group. The *N*-(4-alkoxybenzylidene)-4′-cycloalkylanilines (1), nO.cm series, exhibit more extensive smectic polymorphism than the analogous azomethines (2), cn.Om series, with reversed central linkage.

As expected (see Table VII), comparison of the average *N*-*I* transition temperature for $n/m = 7$–10 reveals that reversal of the CH=N linkage has only a very small effect on nematic thermal stability within each set of benzylideneanilines, and no consistent trend is apparent. In three of the five sets the azomethines (2) have the higher nematic thermal stability but the differences in nematic thermal stability ΔT_{1-2}, are very small in each instance, ranging from 5.1°C to 0.6°C for Ar = cyclo-propyl- and -octyl-phenyl, respectively.

In Figure 7 the average T_{N-I} values for the five sets of benzylideneanilines are plotted against the size (cn or cm) of the cycloalkyl group. As the ring size increases from 3- to 6-membered the nematic thermal stability increases, whereas on changing from a 6- to 7- to an 8- membered ring there is a fall in nematic thermal stability.

Insufficient data are reported in the literature for a similar treatment of the n.Om series. However, for the nO.m series, *N*-*I* transition temperatures[2] for the *n*-propyloxy-*n*-hexyloxy homologues ($n = 3$–6) are available. These have been averaged and the resulting values are shown plotted against the number of carbon atoms in the alkyl group (for $m = 3$–8) in Figure 8 revealing a very different trend to that shown in

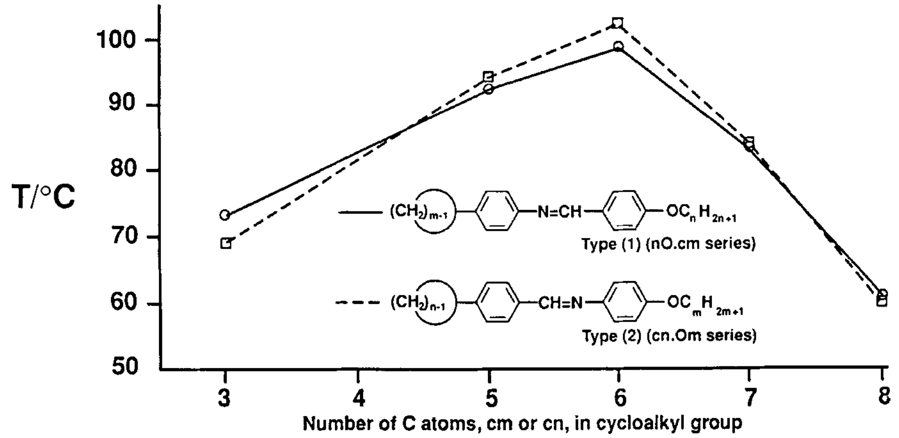


FIGURE 7 Azomethines of Type (1) (nO.cm series) and Type (2) (cn.Om series). Plot of average N-I transition temperature (n/m = 7–10) vs. ring size (cn/cm) of cycloalkyl group.

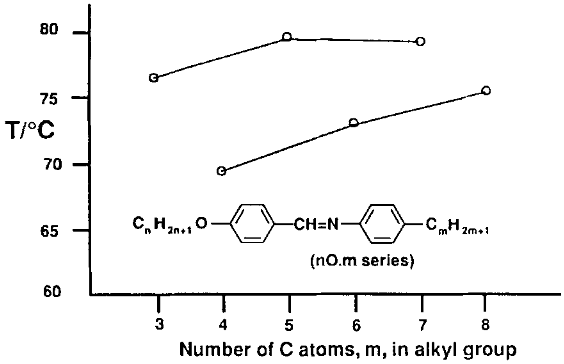


FIGURE 8 Azomethines of nO.m series. Plot of average N-I transition temperature ($n = 3$–6) vs. number of C atoms, m, in alkyl group.

Figure 7 for the nO.cm and cn.Om series. A substantial alternation between odd and even values of *m* occurs, and the points for the average transition temperatures lie on two curves which generally rise as *m* increases. This type of behaviour is commonly observed within an homologous series, the explanation[3] of which is associated with different contributions to the anistropy of molecular polarisability, $\Delta\alpha$, made by successive methylene groups as an alkyl chain is lengthened, assuming a rigid, extended zig-zag alkyl chain.

For the analogous *cyclo*alkyl azomethines (nO.cm and cn.Om series) a different relationship (Figure 7) between cycloalkyl ring size and the nematic thermal stability is clearly evident. In a terminal position, the requirement for the alicyclic ring to preserve linearity of the molecular geometry may be of secondary importance to the maintenance of efficient molecular packing in the mesophase. This may have some of its origin in the flexibility of the conformations adopted by the various terminal alicyclic ring systems which will influence the efficieny of packing of molecules and affect the stability of the liquid crystal phases. A discussion of the role of intermolecular attractive and repulsive (steric) forces in determining the molecular packing and consequent mesomorphic behavior has been given by Osman.[4] With regard to the azomethines of the present work, conformational flexibility of the cycloalkyl group increases on changing from the planar, rigid three-, to the puckered, more mobile five-, to the flexible, six-membered ring system for which the chair conformation is most stable. Seven- and eight-membered ring systems also have very flexible conformational requirements. Seven-membered rings may adopt either a twist-chair or a slightly less favourable twist-boat conformation, both being flexible and readily interconvertible. Eight-membered ring systems belong to the *medium ring* category characterised by the existence of *transannular strain* due to non-bonding interactions across the ring. The extended crown, saddle-shaped, and boat-chair conformations are most favourable with no clearly defined energy difference between the three. However, for the azomethines containing the very flexible seven- and eight-membered ring systems in a terminal position, interconversion of the various possible conformations may only be possible at the expense of an increase in molecular breadth with an associated unfavourable effect on molecular packing in the mesophase. This may explain the observed order of nematic thermal stability, namely, an increase from Ar = cyclo-propyl- to -pentyl- to -hexyl-phenyl followed by a decrease to Ar = cyclo-heptyl- and -octyl-phenyl for each series of benzylideneanilines (1) and (2).

X-Ray diffraction studies of the crystal parameters of selected members of the five homologous series of azomethines may provide further insight into the mode of molecular packing adopted by the cycloalkyl groups.

EXPERIMENTAL

Materials

The azomethines were prepared by standard methods which, together with those used to prepare the cyclopentyl and cyclohexyl derivatives,[1] are described in the following paper.[5]

Physical Measurements

Measurements of transition temperatures and 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.

Acknowledgements

We thank Merck (UK) Ltd. for financial support and SERC for the award of a CASE studentship (M. R.).

References

1. J. W. Brown, D. J. Byron, D. Guillon, X-J. Hong, M. Southcott and R. C. Wilson, *Mol. Cryst. Liq. Cryst.*, **159**, 37 (1988).
2. D. Demus, H. Demus (Vol. I) and H. Zaschke, *Flüssige Kristalle in Tabellen*, VEB Deutscher Verlang für Grundstoffindustrie, German Democratic Republic, Vol. I (1974), Vol. II (1984).
3. W. H. de Jeu, J. van der Veen, and W. J. A. Goossens, *Solid State Commun.*, **12**, 405 (1973).
4. M. A. Osman, *Z. Naturforsch.*, **38a**, 693 (1983).
5. D. J. Byron, A. S. Matharu, M. Rees and R. C. Wilson, *Mol. Cryst. Liq. Cryst.*,