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Mesogenic Oxoheterocycles and Their Benzene Analogues

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To evaluate the effect of terminal five membered oxoheterocyclic (furan) ring on mesomorphism, two simple homologous series (Series A and B) were synthesized. One having an end phenyl ring while other with furyl ring system. The schiff bases were synthesized by using readily available raw materials and simple procedures. Both the series exhibit enantiotropic nematic phases. No smectic mesophase is observed even in higher homologues. The usual odd–even effect is exhibited by both the series.

The mesophase thermal stabilities and the behavior of the two series are compared with each other.

INTRODUCTION

The homologous series with one or more heteroatoms has created a wide interest in liquid crystal field due to their dielectric properties. The heterocyclic mesogens reported so far mainly have nitrogen as a heteroatom[1-3] and mesomorphic compounds with oxygen as a heteroatom are rare.[4,7] Recently more mesogenic homologous series are reported where oxo-heterocyclic system is alicyclic in nature.[8,9] The systematic study of the mesogenic properties of a benzenoid and oxoheterocyclic aromatic system would be interesting. The synthesis of above mentioned oxo-heterocyclic mesogens involve number of stages. Nguyen and Pham[10] have synthesized simple schiff bases with 2-substituted furfural derivatives.

The simple homologous series with oxygen as a heteroatom, Series A, was synthesized and to evaluate the effect of furyl ring on mesomorphism, its benzene analogue (Series B) was also synthesized.

Series A: 4(Furylacryloyloxy)benzylidene-4′-*n*-alkoxyanilines
Series B: 4(Cinnamoyloxy)benzylidene-4′-*n*-alkoxyanilines

EXPERIMENTAL

1. Preparation of Schiff bases

1.1 Furylacrylic acid:[11] Redistilled furfural (0.1 mol) and malonic acid (0.15 mol) were condensed in presence of dry pyridine (20–25 ml) by using few drops of piperidine as a condensing agent. The reaction mixture was heated on a steam-bath for 6 to 8 hrs. It was acidified with cold 1:1 hydrochloric acid, the precipitated acid was filtered and washed with little cold hydrochloric acid, followed by cold water. The acid was crystallized to fine white needles with dilute ethanol. Melting point 140°C. The yield was about 70 percent.

Cinnamic acid used was of H.P.C. quality.

1.2 Furylacryloyl chloride and Cinnamoyl chloride were prepared as per the method described by Dave and Vora for 4-*n*-Alkoxybenzoyl chlorides.[12]

1.3 4(Furylacryloyloxy)benzaldehyde and 4(Cinnamoyloxy)benzaldehyde were synthesized as per the method described by Dave and Kurian[13] for 4(4′-*n*-Alkoxybenzoyloxy)benzaldehydes.

The melting point of 4(Furylacryloyloxy)benzaldehyde: 119°C and the melting point of 4(Cinnamoyloxy)benzaldehyde: 95°C.

The analytical data of both the compounds is satisfactory.

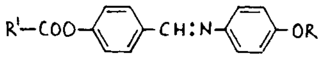
1.4 4-*n*-Alkoxyanilines:[14–16] 4-*n*-Alkoxyanilines can be synthesized by various routes.[14,15] In the present study the method of Criswell and Klandermann[15] was followed as it gives overall better yields of 4-*n*-alkoxyanilines. The boiling points and melting points of all the alkoxyanilines agree well with the values reported in the literature.[15,16]

1.5 Synthesis of Schiff bases: The Schiff bases were synthesized by condensing 4(Furylacryloyloxy)benzaldehyde or 4(Cinnamoyloxy) benzaldehyde with equimolar amount of 4-*n*-alkoxyanilines in ethanol. The Schiff bases were crystallized several times from ethanol until constant transition temperatures were obtained. The transition temperatures are summarized in Table I. The analytical data is satisfactory.

2. Determination of transition temperatures

The melting points and transition temperatures were determined by using Mettler FP-2 polarizing microscope equipped with a heating stage.

TABLE I



Compound No.	*n*-alkyl group R	Transition temperatures °C	
		Nematic	Isotropic
	Series A: R′ = OC_4H_3		
1	Methyl	138.0	220.0
2	Ethyl	128.0	226.0
3	Propyl	117.0	205.0
4	Butyl	122.5	207.0
5	Pentyl	110.0	191.0
6	Hexyl	117.5	196.0
7	Heptyl	94.0	180.0
8	Octyl	103.0	177.0
9	Decyl	98.0	171.0
10	Dodecyl	98.5	162.0
11	Tetradecyl	98.0	153.0
12	Hexadecyl	95.0	145.0
	Series B: R′ = C_6H_5		
13	Methyl	131.5	226.0
14	Ethyl	155.0	234.0
15	Propyl	130.0	219.5
16	Butyl	128.0	216.0
17	Pentyl	118.0	207.0
18	Hexyl	114.0	201.0
19	Heptyl	108.0	198.0
20	Octyl	107.0	192.0
21	Decyl	106.0	179.0
22	Dodecyl	109.0	178.0
23	Tetradecyl	109.0	166.0
24	Hexadecyl	103.0	160.0

RESULTS AND DISCUSSION

Series A: 4(Furylacryloyloxy)benzylidene-4′-*n*-alkoxyanilines

Methoxy to hexadecyloxy derivatives exhibit only nematic mesophase. No smectic mesophase is observed even in higher homologues.

The plot of nematic–isotropic transition temperatures versus the number of carbon atoms in the alkoxy chain (Figure 1) exhibits usual odd–even effect and as the series is ascended the curve shows falling tendency.

Series B: 4(Cinnamoyloxy)benzylidene-4′-*n*-alkoxyanilines

Methoxy to hexadecyloxy derivatives exhibit only nematic phase and as in Series A, no smectic mesophase is observed.

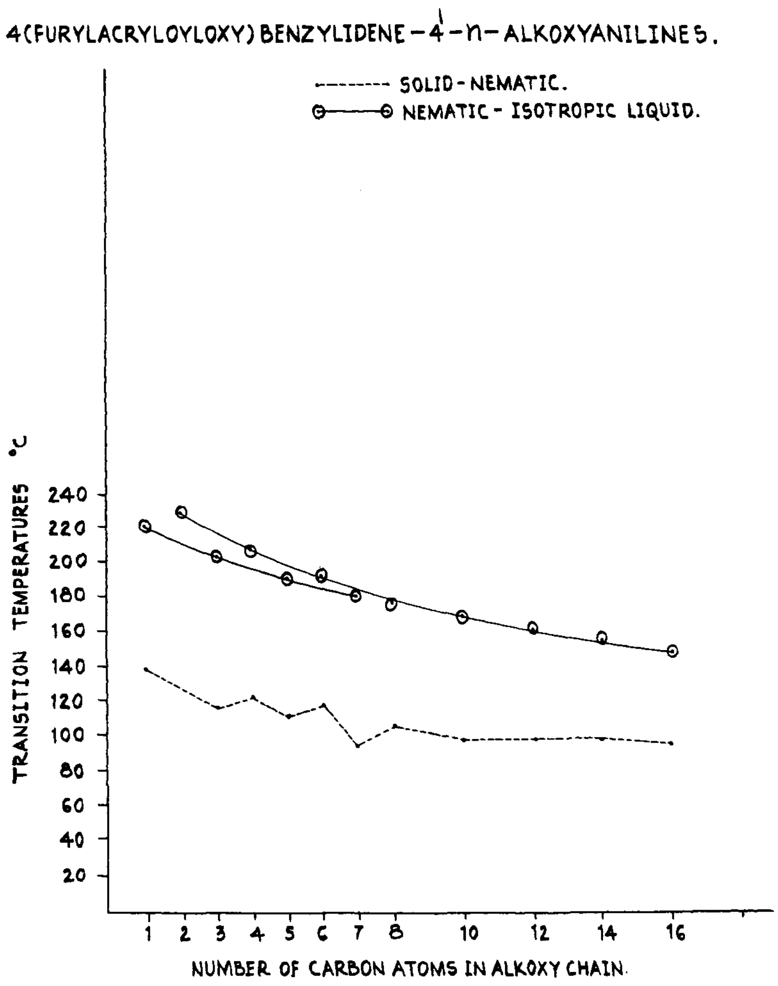


FIGURE 1

The plot of the nematic–isotropic transition temperatures versus the number of carbon atoms in the alkoxy chain (Figure 2) exhibits the odd–even effect up to propoxy derivative and the curve shows falling tendency as the series is ascended.

The geometry of the molecules of both the series are given in Figure 3. The average thermal stabilities of Series A and B are given in Table II.

Reference to Table II indicates that there is a very small difference (12°C) in the nematic thermal stabilities of both the series. This small

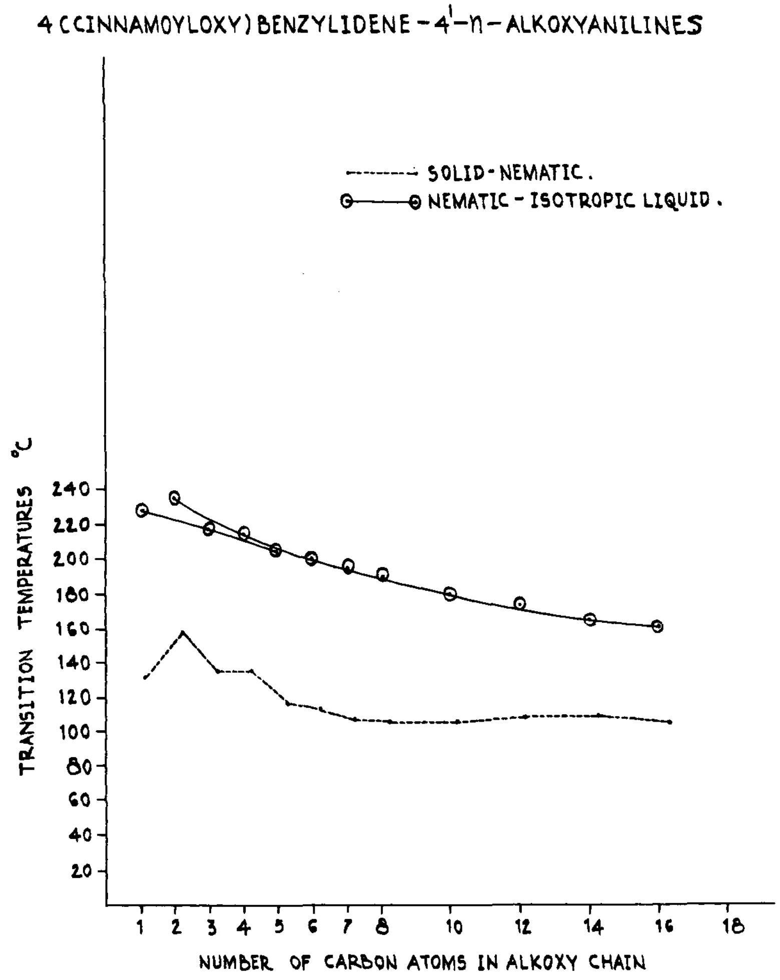


FIGURE 2

TABLE II

Average thermal stabilities

Series	A	B
Nematic–isotropic (C_1–C_{16})	186.0	198.0

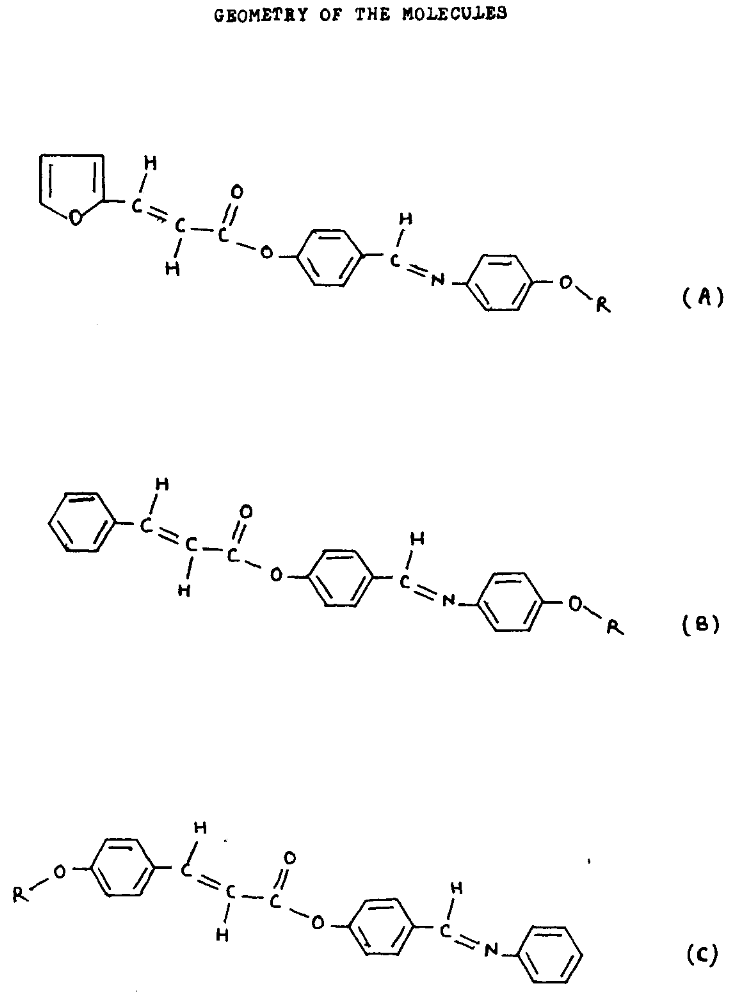


FIGURE 3

difference suggests that even though Series A contains a five membered furan ring, which normally imparts non-linearity, the essential attractive forces are similar to one present in Series B—a benzene analogue. However, the study of the effect of 2,5-disubstituted furan ring on mesogenic behavior compared with the benzene analogue would make interesting observations, as 2,5 substitution would impart non-linearity to a considerable extent.

Oh[17] has reported that all the transition temperatures of pyridine analogues were lower compared with the benzene analogues. In the present study also the furan derivatives have lower transition temperatures. The heteroatom has high electronegativity and will therefore withdraw electrons from the other atoms of the ring system, rendering the ring deactivated related to benzene.

Trivedi and Thaker[7] have reported oxo-heterocyclic mesogenic homologous series, but it is difficult to interpret the effect of oxygen atom as other structural aspects are also different compared with the naphthalene analogues.

By comparing Series A and B, it is obvious that they behave identically except small difference in transition temperatures. Both the series have an alkoxy group at one end and should exhibit smectic mesophases, but none of the members of the series exhibit smectic mesophase. It is difficult to predict the commencement of the smectic mesophases in a homologous series as it depends on the delicate balance of lateral and terminal attractive forces. However, it is difficult to explain the absence of smectic mesophase in series A and B, when series C[18] (Figure 3) exhibits smectic mesophase of comparatively high thermal stability. The molecular skeleton of series B and C is the same differing only in the position of end alkoxy group.

It can be concluded that the replacement of the end phenyl ring by a furan ring does not affect the mesogenic behavior markedly.

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References

1. D. L. Fishel and P. R. Patel, *Mol. Cryst. Liq. Cryst.*, **17**, 139 (1972).
2. J. A. Nash and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **25**, 299 (1974).
3. H. Schubert, Wiss. Z. Univ., Halle, XIX 70M, H5, S1.
4. H. Schubert and K. Hanemann, *Flussige Kristalle in Tabellen*, (VEB Deutscher Verlag, 1972), p. 251.
5. A. I. Pavluchenko, N. I. Smirnova, V. V. Titov, E. I. Kovshev and K. M. Djumeev, *Mol. Cryst. Liq. Cryst.*, **37**, 35 (1976).
6. M. J. S. Dewar and R. M. Riddle, *J. Amer. Chem. Soc.*, **97**, 6658 (1975).
7. N. N. Thaker and K. N. Trivedi, *Indian J. of Chem.*, **20A**, 560 (1981).
8. Howard Sorkin, *Mol. Cryst. Liq. Cryst.*, **56**, 279 (1980).
9. D. Demus and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, **63**, 129 (1981).
10. D. T. Nguyen and T. C. Pham, *Tap. Chi. Hoa. Hoc.*, **14**, 13 (1976).
11. A. I. Vogel, *Textbook of Practical Organic Chemistry* (E.L.B.S. and Longman Group Ltd., 1978), p. 803.

12. J. S. Dave and R. A. Vora, *Liquid Crystals and Ordered Fluids*, eds. J. F. Johnson and R. S. Porter, (Plenum Press, New York, 1970), Vol. 1, p. 477.
13. J. S. Dave and G. Kurian, *J. Phys.* (*Paris*), *Colloq.*, **C1**, 403 (1975).
14. G. N. Vyas and N. M. Shah, *Org. Syn. Coll.*, Vol. IV, (John Wiley and Sons Inc., New York, 1963), p. 836.
15. T. R. Criswell, B. H. Klanderman and B. C. Batesky, *Mol. Cryst. Liq. Cryst.*, **22**, 211 (1973).
16. R. A. Vora and N. Dixit, Presented at Annual Convention of Chemists, Kurukshetra, India, 1979.
17. C. S. Oh, *Mol. Cryst. Liq. Cryst.*, **19**, 95 (1972).
18. Jayrang Dave, Ph.D. Thesis, M.S. University of Baroda, Baroda, India, 1981.