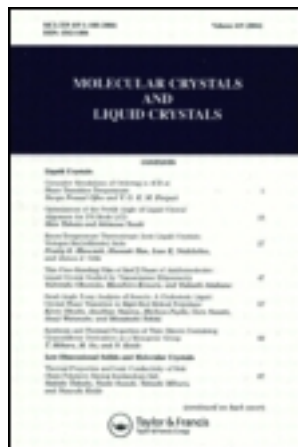


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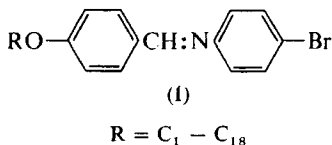
Thermotropic Liquid Crystals I: *p-n*-Alkoxybenzylidene- *p*-Bromoanilines†

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A homologous series (I) of mesomorphic Schiff bases is synthesized by condensing *p-n*-alkoxybenzaldehydes with *p*-bromoaniline.



The first five members are non-mesomorphic. Hexyl to octadecyl derivatives are enantiotropic smectic. The nematic mesophase is not observed in any of the compounds. The series is smectogenic in nature. The plot of transition temperatures versus the number of carbon atoms in the alkyl chain does not show odd-even effect. The smectic-isotropic transition temperature curve shows rising tendency as the series is ascended. It rises to the maximum at the octyl derivative and then levels off. The thermal stabilities of the present series are compared with those of the other related homologous series.

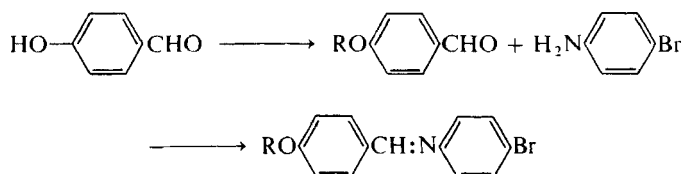
INTRODUCTION

Low melting thermotropic liquid crystals are of great technological importance.¹ Schiff base compounds are synthesized in large numbers as these compounds exhibit nematic and/or smectic mesophases.^{2,3} With a view to exploring the possibility of getting simple liquid crystals the present series has been synthesized and its mesomorphic properties are studied.

† Presented at the Sixth International Liquid Crystal Conference, 23-26 August, 1976, Kent, Ohio, U.S.A.

RESULTS AND DISCUSSION

The compounds are synthesized by the following route:



The melting points and transition temperatures are reported in Table I.

The first five members are non-mesomorphic. Hexyl to octadecyl derivatives exhibit smectic mesophases. Hexyl derivative exhibits polymorphism of the smectic mesophase. The plot of smectic-isotropic transition temperatures versus the number of carbon atoms in the alkyl chain does not show the usual odd-even effect. This is quite an interesting observation as normal nematogenic and smectogenic homologous series exhibit odd-even alternation.

The absence of alternation of the smectic-isotropic transition temperatures in the present series may be attributed to the presence of the bromo group at one end of the molecule which enhances lateral cohesive forces.

The plot of transition temperatures versus the substituent chain length exhibits a tendency for rising smectic-isotropic transition in ascending series.

TABLE I
p-*n*-Alkoxybenzylidene-*p*-bromoanilines
 $\text{RO} \cdot \text{C}_6\text{H}_4\text{CH}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Br}$

Compound	R	Transition temperatures (°C)		
		Smectic II	Smectic I	Isotropic
1.	Methyl	—	—	121.0
2.	Ethyl	—	—	107.0
3.	Propyl	—	—	97.5
4.	Butyl	—	—	102.5
5.	Pentyl	—	—	103.5
6.	Hexyl	76.0	103.0	105.0 ^a
7.	Heptyl	—	95.0	106.5
8.	Octyl	—	102.0	107.5
9.	Nonyl	—	102.0	100.5
10.	Decyl	—	95.0	106.5
11.	Dodecyl	—	85.0	103.0
12.	Tetradecyl	—	81.5	99.0
13.	Hexadecyl	—	86.0	95.0
14.	Octadecyl	—	85.0	90.0

^a Arora, *et al.*,⁴ reports K 74.0°C S_{II} 103.0°C S_I 105.5°C I.

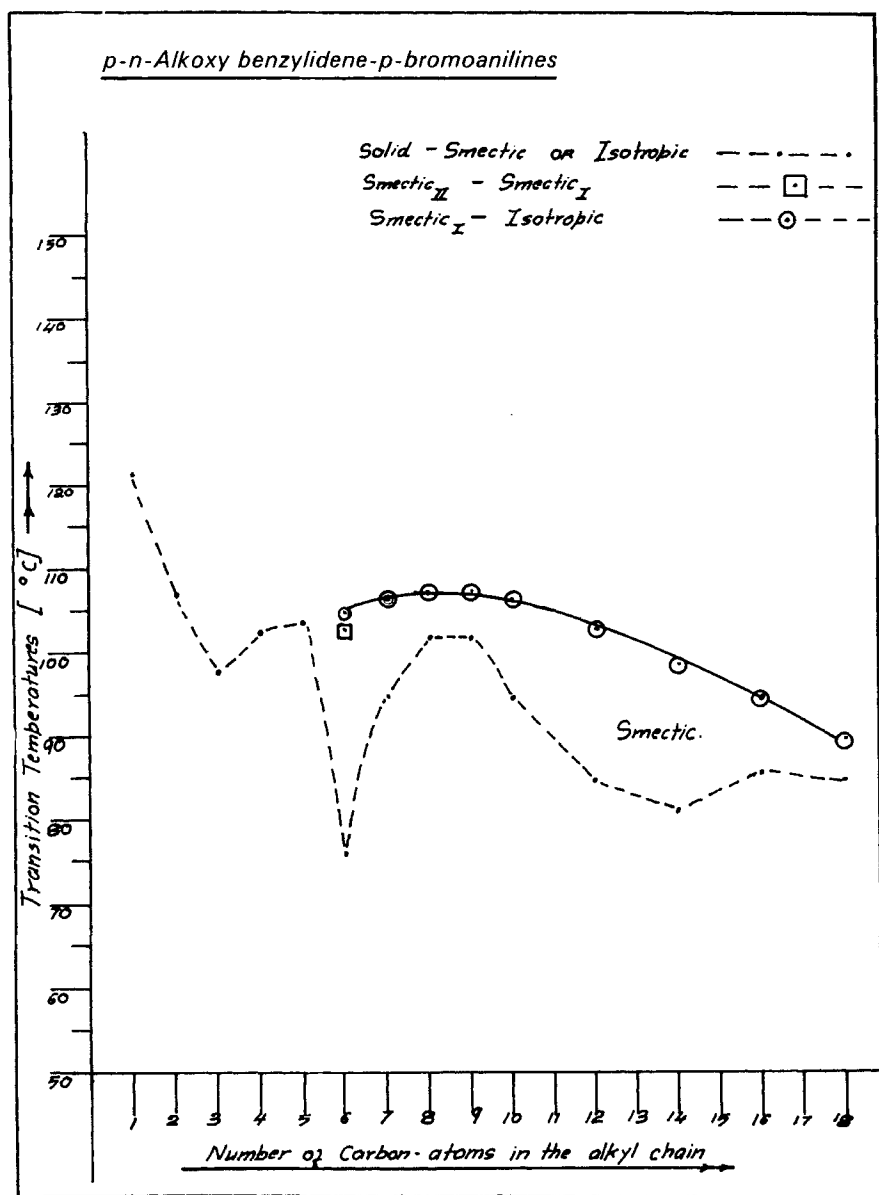


FIGURE 1

This type of behavior is often observed in the homologous series having low transition temperatures.^{5,6}

The average thermal stabilities of the present series are higher compared to those of the series ethyl (*p*-*n*-alkoxybenzylidene-*p*-aminobenzoates)⁷ and *p*-*n*-alkoxybenzylidene-*p*'-ethylanilines.⁸

MATERIALS AND METHODS

Melting points and transition temperatures were determined by using a thermopan polarising microscope equipped with a heating stage. The smectic I phase exhibited fan-shaped texture in all the compounds.

PREPARATION OF COMPOUNDS

1 *p*-*n*-Alkoxybenzaldehydes

These were prepared by the method of Gray.⁹ Boiling points compare well with the literature.

2 Schiff bases

Schiff base compounds were prepared by refluxing *p*-*n*-alkoxy-benzaldehydes (1.0 mol) with *p*-bromoaniline (1.0 mol) in ethyl alcohol for about one hour and recrystallizing the product several times from methanol or acetone into fine needles or plates, which gave sharp melting points and transition temperatures. The analysis of all the compounds was satisfactory. The analytical data of some representative compounds are summarized in Table II. Yields were about 80%.

TABLE II
p-*n*-Alkoxybenzylidene-*p*-bromoanilines

Sr. No.	Alkyl group	Molecular formula	% Required			% Found		
			C	H	N	C	H	N
1.	Methyl	C ₁₅ H ₁₄ BrNO	59.21	4.60	4.60	59.44	4.38	5.10
2.	Octyl	C ₂₁ H ₂₆ BrNO	64.95	6.70	3.61	65.37	6.91	3.23
3.	Octadecyl	C ₃₁ H ₄₆ BrNO	70.46	8.71	2.61	69.96	8.41	2.85

Acknowledgement

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