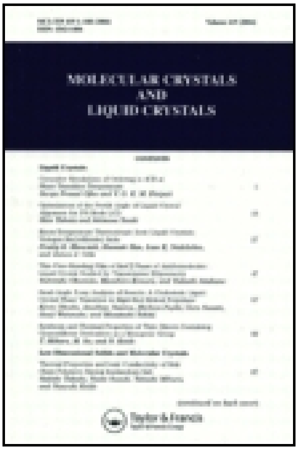

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N. H. Shah [a] , R. A. Vora [a] & N. D. Jadav [a]
[a] Applied Chemistry Department, Faculty of Technology & Engineering, M. S. University of Baroda, Baroda, 390 001, India

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Azomesogens: (I) 4-(4′-n-Alkoxy-2′-Methylphenylazo)—Benzoic acids: (II) Ethyl 4-(4′-n-Alkoxyphenylazo)—Benzoates

N. H. SHAH, R. A. VORA and N. D. JADAV

Applied Chemistry Department, Faculty of Technology & Engineering, M. S. University of Baroda, Baroda: 390 001 (India)

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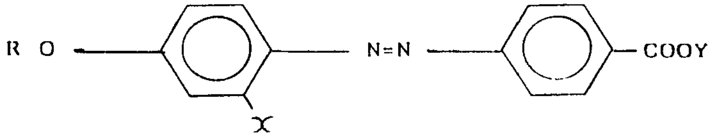
Two mesongenic homologous series containing azo group are synthesized.



		X	Y
Series	I.	CH_3	H
	II.	H	CH_3
	III.	H	C_2H_5
	IV.	H	C_3H_7

The esters of Series II, III and IV exhibit only the smectic phase. The smectic phase exhibits focal conic or fan-shaped textures. Members of Series I exhibit nematic phases, whereas the members of Series II and IV exhibit enantiotropic smectic phase with one exception. The members of series IV exhibit odd-even effects for smectic-isotropic transition temperatures.

The smectic phase appears ~70° to 90° C. The thermal stabilities and structural aspects are discussed in detail. All the compounds were characterised by standard methods. The visible spectra helped to obtain λ_{max} of the mesogens.

Keywords: azo linkage, benzoates, smectics

INTRODUCTION

Azodyes are used in guest host interaction.[1-8] Earlier we had reported a couple of mesogenic homologous series with azo central linkage. In continuation of our work, a couple of more homologous series are synthesized in the present study.

EXPERIMENTAL

Synthesis of 4-(4′-hydroxy-2′-methylphenylazo)—benzoic acid, ethyl 4-(4′-hydroxyphenylazo)—benzoate and their alkylation was carried out by known methods.[10-12] All of the compounds were analysed by elemental analysis and IR spectra. The transition temperatures were determined by using a Laborlux polarising microscope provided with a hot stage. The data are recorded in Tables I and II.

RESULTS AND DISCUSSION

Series I: 4-(4′-n-Alkoxy-2′-Methylphenylazo) Benzoic Acids

All the members of the series exhibit nematic mesomorphism. The smectic mesophase does not commence even at the last member of the series. The nematic mesophase is of very high thermal stability. The melting points and the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (Figure 1).

The nematic-isotropic transition temperature curve exhibits usual odd-even ef-

TABLE I

Transition temperatures of series I

Compound	R = $(CH_2)_nCH_3$			**Transition temperatures °C.**		
No.	**n**	**x**	**y**	**S**	**N**	**I**
Series I.						
1.	0	CH_3	H	-	230.00	246.00 (d)
2.	1	CH_3	H	-	211.00	257.00
3.	2	CH_3	H	-	203.00	228.00
4.	3	CH_3	H	-	192.00	235.00
5.	4	CH_3	H	-	182.00	227.00
6.	5	CH_3	H	-	172.00	223.00
7.	6	CH_3	H	-	170.00	220.00
8.	7	CH_3	H	-	163.00	218.00
9.	9	CH_3	H	-	158.00	211.00
10.	11	CH_3	H	-	155.00	202.00
11.	13	CH_3	H	-	155.00	201.00
12.	15	CH_3	H	-	160.00	292.00
13.	17	CH_3	H	-	155.00	176.00

TABLE II

Transition temperatures of series II

Compound	R = $(CH_2)_nCH_3$			Transition temperatures °C.		
No.	n	x	y	S	N	I
Series II.						
14.	0	H	C_2H_5	-	-	103.00
15.	1	H	C_2H_5	-	-	111.00
16.	2	H	C_2H_5	-	-	105.00
17.	3	H	C_2H_2	-	-	82.00
18.	4	H	C_2H_5	(85.00)*	-	90.00
19.	5	H	C_2H_5	92.00	-	100.00
20.	6	H	C_2H_5	76.00	-	102.00
21.	7	H	C_2H_2	85.00	-	105.50
22.	9	H	C_2H_5	100.00	-	104.00
23.	11	H	C_2H_5	92.00	-	102.00
24.	13	H	C_2H_5	88.00	-	99.00
25.	15	H	C_2H_5	85.00	-	98.00
26.	17	H	C_2H_5	78.00	-	94.00

* Values in the parentheses indicate monotropy. All the alkoxy groups are normal.

fects and falls steadily for the middle members. It almost levels up between dodecyloxy and tetradecyloxy members and then again it falls.

Table III summarizes the average thermal stabilities and comparative geometry of the present series (I). These are compared with those of p-n-alkoxybenzilidene-p aminobenzoic acids, A[13] and 4-n-alkoxydiphenyl-4-carboxylic acids B.[14]

Table I shows that nematic thermal stabilities of the present series I are lower compared to those of series A and B. Compared to series B, the series I is a little longer and more polarizable, but has less linearity and increased breadth due to the lateral methyl group. It is evident that increase in breadth and thickness predominates, resulting in lower thermal stabilities of series I. Compared to series A, the present series is a little more polarizable but the length is almost equal. Again, the breadth-increasing effect of the lateral methyl group in the dimer of the acid predominates and results in lowering the thermal stabilities of series I.

Decrease in nematic thermal stability is not to pronounced compared to series A, but the smectic mesophase is completely eliminated from the present series. Looking to the length of the acid dimer, the methyl group should not have much deterrent effect on the smectic mesophase. This suggests that methyl group ortho to azo linkage is causing steric hindrance, which may result in more deviation from linearity, hence the overall geometry of the molecules of series I would be such

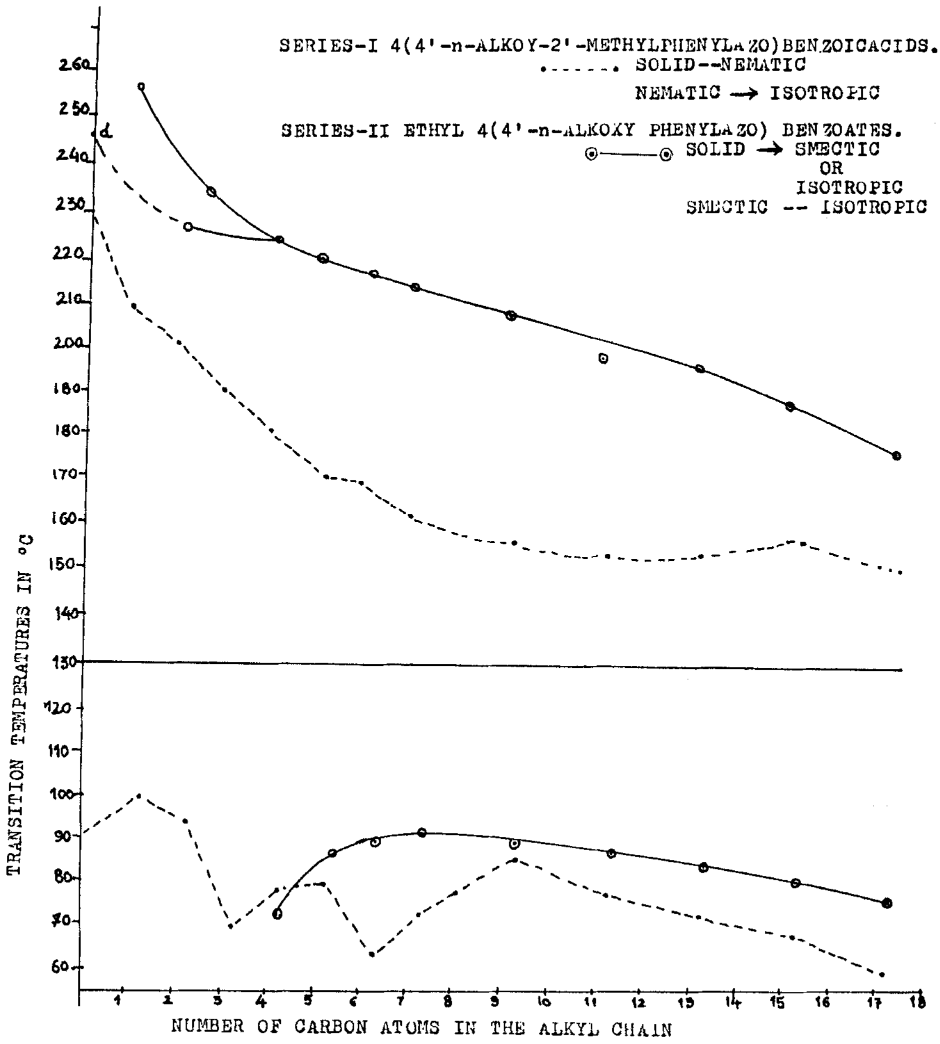


FIGURE 1

that it would not be favouring close packing of the molecules. This close packing of the molecules is one of the requirements for the commencement of the smectic mesophase.

Series II: Ethyl 4-(4′-n-Alkoxyphenylazo)—Benzoates

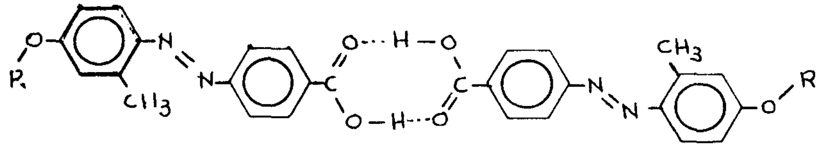
Smectic mesophase commences at the pentyloxy member as a monotropic phase. Hexyloxy-to-octadecyloxy members are enantiotropic smectic. The smectic phase inferred from their texture appearance is of smetic A type.

A plot of smectic-isotropic transition temperatures versus the number of carbon atoms in the alkyl chain does not show usual odd-even effects (Figure 1). The plot of transition temperatures versus the substituent chain length exhibits a tendency to raise smectic-isotropic transition temperatures in ascending series. It rises to the

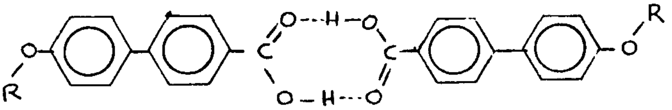
TABLE III

Average thermal stabilities

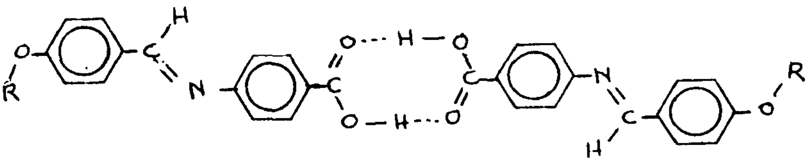
SERIES.....	I	II	A	B	C	D	E
Nematic-Isotropic.	223.0	-	272.0	252.0	-	-	-
Smectic-Isotropic.	-	103.0	-	-	113.5	97.7	96.7



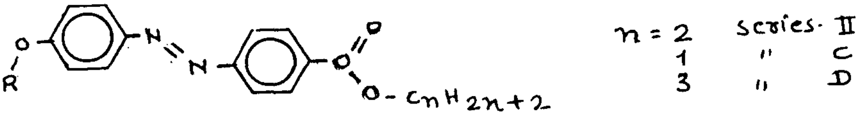
I



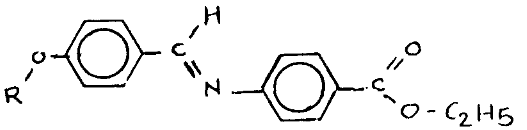
A



B



II



E

maximum and then levels off. Table III summarizes the average smectic thermal stabilities and comparative geometry of the series II and these are compared with methyl series C and n-propyl series D reported by us[9] earlier and with those of ethyl 4-n-alkoxybenzylidene-4-aminobenzoates series E.[15]

Reference to Table III indicates that thermal stabilities of series II is between series C and D. The esters homologues are changed from CH_3 to n-C_3H_7 hence one cannot expect much change in thermal stabilities. However, the mesogenic tendency increases as one goes from methyl to propyl esters. In the case of series

C only four members are mesogenic, exhibiting monotropic phases. In the case of series II and D, enantiotropic smectic mesophases are observed in more homologue.

The smectic thermal stabilities of series II and series E are almost the same. This is understandable as there is not much change in the geometry of the two series, the central linkages are changed from N=N to —CH=N—, respectively. The transition temperatures of series II (Table II) are much lower than compared to series I having carboxylic therminal group. The formation of dimer and higher thermal stabilities of series I is explained earlier.

Acknowledgment

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