

Azomesogens with 1,2,4-trisubstituted benzene moiety[†]

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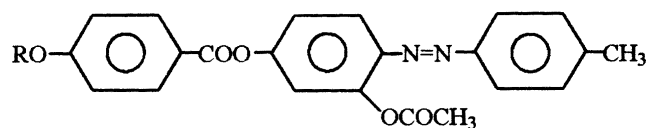
Abstract. New mesogenic homologous series having an azo central linkage was synthesized by fixing a rigid 4-methyl phenyl azo group to resorcinol moiety. The terminal and lateral phenolic –OH groups were esterified, one by one, with 4-*n*-alkoxybenzoyl and acetyl group, respectively. All the twelve homologues synthesized exhibit mesomorphism. The methoxy to *n*-decyloxy and *n*-hexadecyloxy derivatives exhibit monotropic nematic mesophase whereas, *n*-dodecyloxy and *n*-tetradecyloxy derivatives exhibit enantiotropic nematic mesophase. The mesogenic properties of the present series was compared with those of other structurally related mesogenic series.

Keywords. 1,2,4-Trisubstituted benzene; lateral acetyloxy group; nematic mesophase.

1. Introduction

Until 1983 it was generally accepted that lateral substituents diminish the mesogenic property of a compound, the extent of the effect depending on their size. As found by Weissflog and Demus (1983, 1984), surprisingly, compounds with large flexible lateral substituents exhibit liquid crystalline phases. They also reported (Weissflog and Demus 1985) compounds containing two long chain lateral substituents that are nematic. Cox *et al* (1984) synthesized nematogens in which lateral phenyl group is attached without a spacer. Gallardo and Muller (1984), Weissflog and Demus (1988) and Weissflog *et al* (1986, 1990) also reported mesogens with lateral aromatic substituents. Subsequently number of homologous series with trisubstituted benzene nucleus have appeared in the literature (Baumeister *et al* 1990; Diele *et al* 1991; Berdague *et al* 1995; Weissflog *et al* 1996; Weissflog and Jacobi 1997; Perez *et al* 1997). Recently, we reported (Vora *et al* 2001) four mesogenic homologous series containing three rings in the main core and substituted by a lateral aromatic branch or hydroxy group on the central benzene nucleus. The mesogenic homologous series with lateral hydroxy group exhibited nematic mesomorphism whereas homologous series with lateral aromatic branch exhibited smectogenic tendencies. In the present work, we have introduced lateral acetyloxy group in order to study the effect of such a group on the mesomorphic properties and transition temperatures as this group will lower the transition temperatures. Further, the effect of lateral

acetyloxy group has not been studied extensively and this prompted us to carry out the present work.



Series I.

2. Experimental

2.1 Characterization

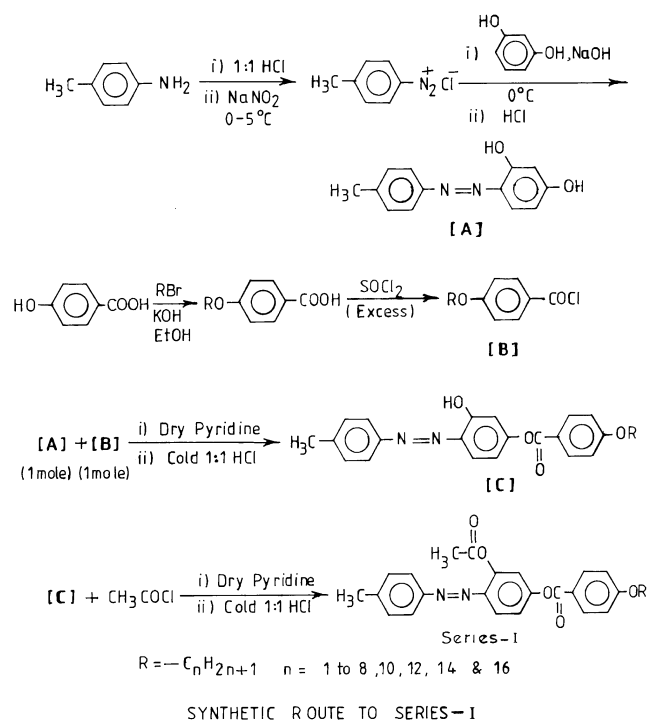
Microanalysis of the compounds were performed on a Coleman carbon-hydrogen analyser, and IR spectra were recorded on Shimadzu IR-408 using KBr pellets. ¹H NMR spectra were recorded on a Perkin-Elmer R-32 spectrometer using TMS as a standard. The calorimetric studies were carried out on a Mettler TA 4000 DSC apparatus by adopting a scanning rate of 5°C/min. Liquid crystalline properties were investigated on a Leitz Laboulux 12 POL microscope provided with a heating stage.

2.2 Synthesis

4-Hydroxybenzoic acid, the appropriate *n*-alkylhalides (BDH), resorcinol, *p*-toluidine and thionyl chloride (Sisco Chem.) were used as received. All the solvents were dried and distilled prior to use. The compounds of the new series I were prepared following the pathway shown in scheme 1.

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Scheme 1.

2.2a *4-Methyl 2-(4-hydroxy) azobenzene (A)*: This compound was synthesized by using conventional method of diazotization and coupling (Vogel 1989).

2.2b *4-n-Alkoxybenzoyl chloride (B) and 4-methyl 2-(4-hydroxy 4-(4ⁿ-alkoxybenzoyloxy) azobenzenes (C)*: The synthesis of these compounds is described elsewhere (Vora *et al* 2001).

2.2c *General procedure for synthesis of series I compounds*: Compound C (10 mmol) was dissolved in dry pyridine (15 ml) and added slowly into acetyl chloride

(10 mmol) in dry pyridine (15 ml) below 15°C. The mixture was then heated on a water bath for 1 h and was allowed to stand overnight at room temperature. It was acidified with cold 1 : 1 aqueous hydrochloric acid. The solid was separated, dried and triturated by stirring for 30 min with 10% aqueous sodium hydroxide solution and washed with water. The insoluble product was thus separated from the reactants. Finally all the products were crystallized from alcohol till constant transition temperatures were obtained. The elemental analysis (table 1) of all the compounds was found to be satisfactory. IR and ¹H NMR spectral data of *n*-butyloxy derivative of series I are given below.

IR (KBr) spectra (ν_{\max} , cm⁻¹): 2950, 1760, 1720 (–COO–), 1605 (–N=N–), 1505, 1465, 1365, 1250, 1230, 1200, 1165, 835, 755.

¹H NMR spectra (Solvent CDCl₃, 60 MHz): *d* 0.9 (*t*, 3H, –CH₃), 1.4–1.7 (*m*, 4H, 2*x* –CH₂–), 2.3 (*s*, 3H, –PhCH₃), 2.4 (*s*, 3H, –OCOCH₃), 4.0 (*t*, 2H, –OCH₂–), 6.8–7.2 (*m*, 5H at C–3', C–5', C–3, C–5 and C–6'), 7.6–8.0 (*m*, 4H at C–3'', C–5'', C–2 and C–6), 8.0–8.2 (*d*, 9 Hz, 2H at C–2'' and C–6'').

3. Results and discussion

The transition temperatures for compounds of series I are recorded in table 2. Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results, therefore, we may draw conclusions concerning the nature of the phases which occur during the transitions. In the present study, enthalpies of *n*-dodecyloxy and *n*-tetradecyloxy derivatives were measured by differential scanning calorimetry. Data are recorded in table 3. Enthalpy values of the nematic phase transitions agree well with the literature value (Marzotko and Demus 1975) which has helped in further confirmation of meso-phase type.

Table 1. Elemental data of series I.

Compound no.	R = –C _n H _{2n+1} F n =	Formula	Required (%)			Found (%)		
			C	H	N	C	H	N
1	1	C ₂₂ H ₂₀ N ₂ O ₅	68.32	4.95	6.93	68.14	5.06	6.45
2	2	C ₂₃ H ₂₂ N ₂ O ₅	68.90	5.26	6.70	68.66	5.49	6.91
3	3	C ₂₄ H ₂₄ N ₂ O ₅	69.44	5.55	6.48	69.83	5.78	6.27
4	4	C ₂₅ H ₂₆ N ₂ O ₅	69.95	5.83	6.28	70.03	5.84	5.97
5	5	C ₂₆ H ₂₈ N ₂ O ₅	70.43	6.09	6.09	70.14	6.38	6.24
6	6	C ₂₇ H ₃₀ N ₂ O ₅	70.89	6.33	5.91	70.88	6.55	5.55
7	7	C ₂₈ H ₃₂ N ₂ O ₅	71.13	6.56	5.74	71.70	6.89	5.37
8	8	C ₂₉ H ₃₄ N ₂ O ₅	71.71	6.77	5.58	71.64	6.94	5.26
9	10	C ₃₁ H ₃₈ N ₂ O ₅	72.45	7.17	5.28	72.00	7.09	5.61
10	12	C ₃₂ H ₄₂ N ₂ O ₅	73.12	7.53	5.02	73.23	7.97	4.85
11	14	C ₃₅ H ₄₆ N ₂ O ₅	73.72	7.85	4.78	73.64	7.71	4.86
12	16	C ₃₇ H ₅₀ N ₂ O ₅	74.27	8.14	4.56	74.56	7.88	4.14

3.1 Series I: 4-Methyl 2-(acetyloxy 4-(4²-n-alkoxybenzoyloxy) azobenzenes

Twelve homologues have been synthesized. They are purely nematogenic. All the homologues of this series

Table 2. Transition temperatures (°C) of the present series I.

Compound no.	$R = C_nH_{2n+1}$ $n =$	Transition temperatures (°C)		
		Cr	N	I
1	1	• 156.0	(• 125.0)	•
2	2	• 148.0	(• 129.0)	•
3	3	• 134.0	(• 104.0)	•
4	4	• 128.0	(• 119.0)	•
5	5	• 121.0	(• 93.0)	•
6	6	• 148.0	(• 103.0)	•
7	7	• 125.0	(• 97.0)	•
8	8	• 102.0	(• 94.0)	•
9	10	• 101.0	(• 92.5)	•
10	12	• 87.5	• 91.0	•
11	14	• 78.0	• 90.0	•
12	16	• 104.0	(• 87.0)	•

(•) Monotropic value; Cr = crystalline phase; N = nematic phase; I = isotropic liquid phase.

Table 3. DSC data.

Compound no. (table 1)	Transition	$\Delta H/Jg^{-1}$	$\Delta S/Jg^{-1}k^{-1}$
10	Cr-N	45.64	0.1274
	N-I	00.26	0.0007
11	Cr-N	49.38	0.1408
	N-I	00.33	0.0009

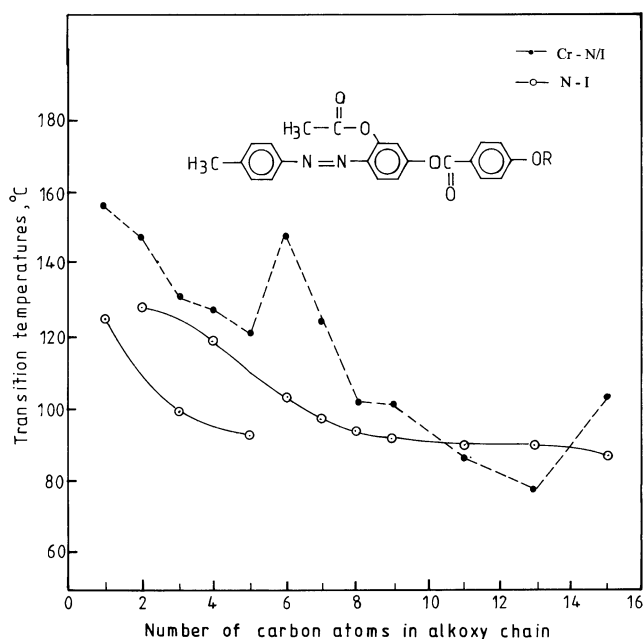


Figure 1. The phase behaviour of series I.

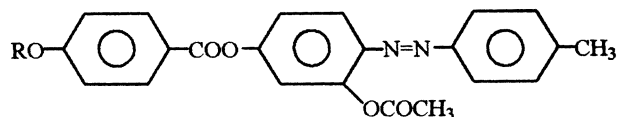
exhibit monotropic nematic mesophase except the *n*-dodecyloxy- and *n*-tetradecyloxy homologues which are enantiotropic nematic.

It is clear from the plot of transition temperatures against the number of carbon atoms in the alkoxy chain (figure 1) that the nematic-isotropic transition temperatures exhibit the usual alternations associated with homologous series of mesomorphic ethers containing alkyl chain. Hence these transition points lie on two falling curves, the upper one determined by those ethers containing an even number of carbon atoms, and the lower by those with an odd number of carbons in the alkoxy chain. As a result of this alternation, the highest nematic-isotropic transition temperature found for ethyl ether is 129°C.

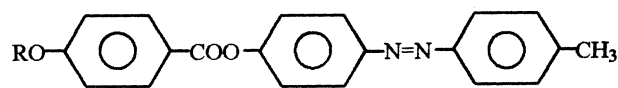
Table 4 summarizes the average thermal stabilities and molecular structures of the present series I and the structurally related series A (Zaschke *et al* 1975), B and C (Vora *et al* 2001). The average nematic thermal stability of the present series I is lower than those of series A. Compared with the molecules of series A, the molecules of series I have increased breadth due to the lateral acetyloxy (CH₃COO-) group on the central benzene ring. There are several reports in the literature (Gray 1966, 1976, 1979; Coates 1990; Demus and Hauser 1990) which

Table 4. Average thermal stabilities (°C).

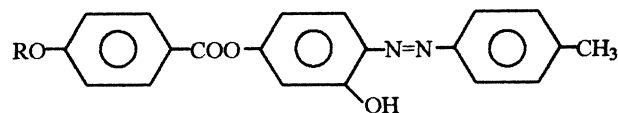
Series	I	A	B	C
SmC/N-I (C ₄ -C ₈)	101.2	227.8	233.0	39.2
Commencement of smectic phase	-	-	-	C ₄



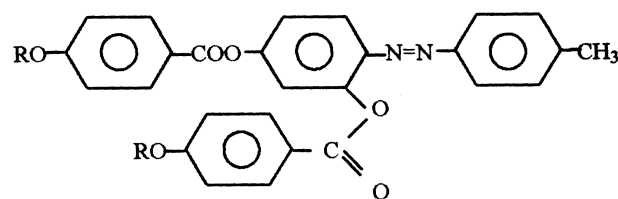
Series I



Series A



Series B



Series C

Molecular structures of the compounds of series I, A, B and C.

prove that the lateral substituents depress the thermal stabilities of the compounds, hence the average nematic thermal stability is lower in the present series I.

Reference to table 4 indicates that the average nematic thermal stability of series I is higher than that of series B. The molecules of series I and B differ only at lateral substituent. Series I has a lateral acetyloxy group whereas series B has a hydroxy group at that position. Due to the intramolecular association of lateral hydroxy group with an azo central linkage it is less effective in broadening of the molecules of series B whereas the effect of increase in breadth is prominent in series I because of the lateral acetyloxy group. Therefore, the average nematic thermal stability of series I is lower in the present series I.

Series C exhibits smectic C mesophase whereas series I exhibits only nematic mesophase. Hartung *et al* (1995) suggested packing of such molecules in series C. The molecules are arranged in lamellar sheets which are characterized by a parallel molecular alignment with an interlocking of neighbouring molecules by their bulky branches and intercalation of the alkyl chains. However, the existence of a lateral motif in the present series I induces the nematic phase, preventing the more ordered in plane molecular association needed for smectic arrangement as observed in number of homologous series (Weissflog *et al* 1996). Hence the present series I exhibits only nematic mesophase.

4. Conclusions

New mesogenic homologous series with lateral acetyloxy group on central benzene nucleus were synthesized. The study indicated that the lateral acetyloxy group adversely affects the mesophase thermal stabilities. However, the short aliphatic chain can stabilize the nematic phase whereas long aromatic lateral substituents stabilize smectic phases.

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References

- Baumeister U, Kosturkiewicz Z, Hartung H, Weissflog W and Demus D 1990 *Liq. Cryst.* **7** 241
- Berdague P, Perez F, Judeinstein P and Bayle J P 1995 *New J. Chem.* **19** 293
- Coates D 1990 in *Liquid crystals, applications and uses* (ed.) B Bahadur (Singapore: World Scientific) Vol. **1**, Ch. 3
- Cox R, Volksen W and Dawson B L 1984 in *Liquid crystals and ordered fluids* (eds) A C Griffin and J F Johnson (New York: Plenum) Vol. **4**, p. 33
- Demus D and Hauser A 1990 in *Selected topics in liquid crystal research* (ed.) H D Koswig (Berlin: Akademie-Verlag) p. 19
- Diele S, Madicke A, Knauff K, Neutzler J, Weissflog W and Demus D 1991 *Liq. Cryst.* **10** 47
- Gallardo V and Muller H J 1984 *Mol. Cryst. Liq. Cryst.* **102** 13
- Gray G W 1966 *Mol. Cryst.* **1** 333
- Gray G W 1976 in *Advances in liquid crystals* (ed.) G H Brown (New York: Academic Press) Vol. **2**, p. 1
- Gray G W 1979 in *The molecular physics of liquid crystals* (eds) G R Luckhurst and G W Gray (London: Academic Press) Chs 1 & 12
- Hartung H, Hofmann F, Stutzer C and Weissflog W 1995 *Liq. Cryst.* **19** 839
- Marzotko D and Demus D 1975 *Pramana – Suppl.* 189
- Perez F, Judeinstein P, Bayle J P, Roussel F and Fung B M 1997 *Liq. Cryst.* **22** 711
- Vogel A I 1989 in *Text book of practical organic chemistry* (London: ELBS and Longmann) 5th ed. p. 946
- Vora R A, Prajapati A K, Kevat J B and Raina K K 2001 *Liq. Cryst.* **28** 983
- Weissflog W and Demus D 1983 *Cryst. Res. Technol.* **18** K21
- Weissflog W and Demus D 1984 *Cryst. Res. Technol.* **19** 55
- Weissflog W and Demus D 1985 *Mater. Chem. Phys.* **12** 461
- Weissflog W and Demus D 1988 *Liq. Cryst.* **3** 275
- Weissflog W and Jacobi A 1997 *Mol. Cryst. Liq. Cryst.* **304** 15
- Weissflog W, Diele S, Pelzl G, Manke H and Demus D 1986 *Liq. Cryst.* **1** 101
- Weissflog W, Demus D and Diele S 1990 *Mol. Cryst. Liq. Cryst.* **191** 9
- Weissflog W, Wiegeleben A, Haddawi S and Demus D 1996 *Mol. Cryst. Liq. Cryst.* **281** 15
- Zaschke H, Debacq J and Schubfrt H 1975 *Z. Chem.* **15** 100