Molecular Crystals and Liquid Crystals

Azomesogens Having a Lateral Hydroxy Substituent

Sandhya Dixit [a] & R. A. Vora [a]

[a] Department of Applied Chemistry, Faculty of Technology and Engineering, The M. S. University of Baroda, Kalabhavan, Vadodara, India

Version of record first published: 18 Mar 2009

To cite this article: Sandhya Dixit & R. A. Vora (2009): Azomesogens Having a Lateral Hydroxy Substituent, Molecular Crystals and Liquid Crystals, 501:1, 43-52

To link to this article: http://dx.doi.org/10.1080/15421400802697236

Mol. Cryst. Liq. Cryst., Vol. 501, pp. 43–52, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802697236

Azomesogens Having a Lateral Hydroxy Substituent

Sandhya Dixit and R. A. Vora
Department of Applied Chemistry, Faculty of Technology
and Engineering, The M. S. University of Baroda, Kalabhavan,
Vadodara, India

Two homologous series of liquid crystalline azoesters consisting of a lateral hydroxyl substituent on the central benzene ring at 2′ positions have been synthesized and thermally characterized. All the 24 members, of both series, exhibit high temperature nematic phases. All the compounds of both series are thermally stable and exhibit a wide mesomorphic range. The homologues have been characterized using Infra Red (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), and Differential Scanning Calorimetry (DSC). Their mesomorphic properties and other characteristics are discussed.

Keywords: azomesogens; mesomorphism; nematic; smectic

INTRODUCTION

Azo dye liquid crystals have attracted much attention for potential use in optical storage applications because of their easy availability, reasonable photo-fatigue resistance, and the marked transformation of their molecular shape up on E to Z photoisomerization [1–7]. Azodyes have a reasonable dichroic ratio for reflective liquid crystal device which are of considerable interest owing to their remarkably lower power consumption [8].

Until early 1970s, it was believed that compounds with terminal phenolic or amino groups would not be conducive to mesomorphism due to intermolecular hydrogen bonding which would lead to nonlinear arrangement of molecules. Schroeder and Schroeder [9] reported a few terminally hydroxyl substituted mesogens. Vora and Gupta [10] for the

Address correspondence to Sandhya Dixit, Department of Applied Chemistry, Faculty of Technology and Engineering, The M. S. University of Baroda, P.O. Box 51, Kalabhavan, Vadodara 390-001, India. E-mail: snddxt_20@yahoo.com

first time reported mesogenic homologous series with terminal and lateral hydroxyl groups. Subsequently, a few more such homologous series with lateral hydroxyl groups have been reported [11–13]. In the present study, two mesogenic homologous series [series I and II] containing a lateral hydroxyl group have been synthesized.

EXPERIMENTAL

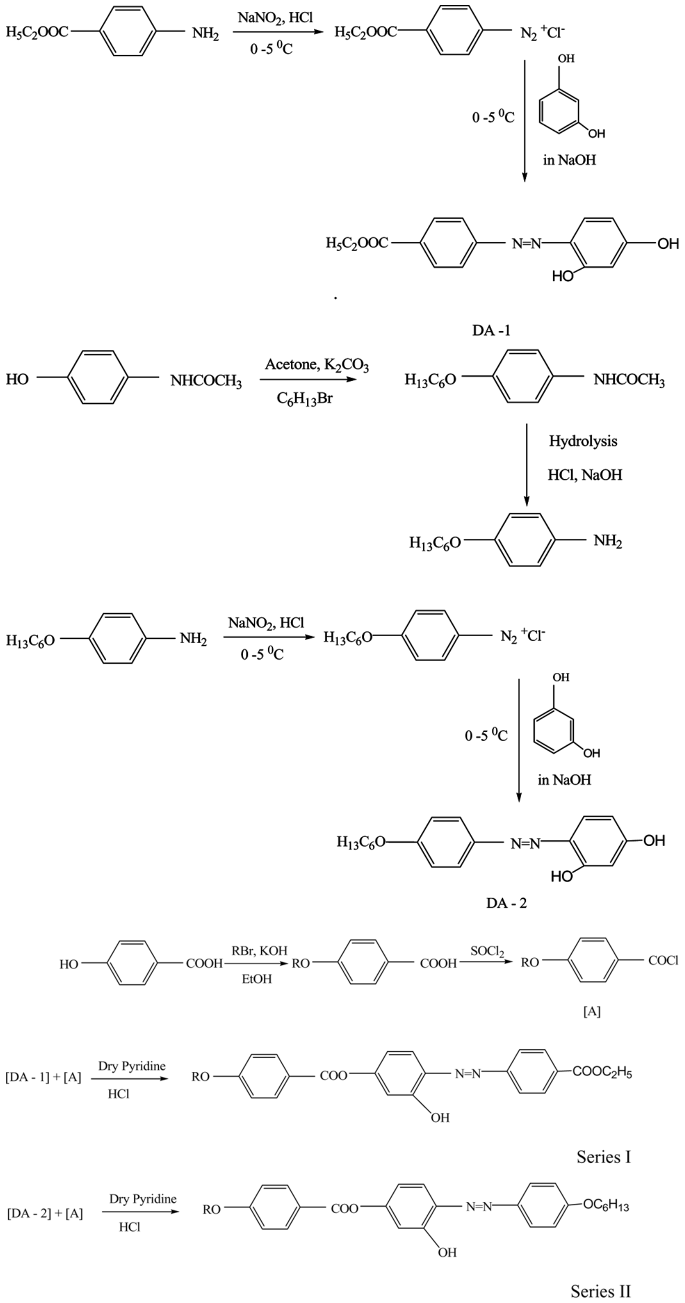
Characterisation

Microanalysis of the compounds were performed on a Coleman carbon–hydrogen analyzer, and they were in conformity with the theoretical values. IR spectra were recorded on a Perkin-Elmer spectrophotometer and Nicolet Impact 400 FTIR. ^{1}H NMR Spectra were recorded on a Perkin-Elmer (90 MHz) and (60 MHz) spectrometers. The liquid crystalline properties were investigated on a Leitz–Labourlux 12 POL microscope provided with a heating stage. DSC was investigated on a Metler TA-4000 system.

Synthesis of Series I and II

4-Hydroxy benzoic acid, the appropriate n-alkyl halides, ethyl-p-aminobenzoate, and paracetamol were used as received. Solvents were dried and distilled prior to use. The route of synthesis for series I and II is illustrated in the Scheme 1.

4-n-hexyloxy aniline was synthesized by reported methods [14,15]. 4-Carbethoxy-2′-4′-dihydroxy azobenzene (DA-1) and 4-n-hexyloxy-2’4’-dihydroxy azobenzene (DA-2) were synthesized using conventional methods of diazotization and coupling [16]. 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [17]. The two series, namely, 4-carbethoxy-[2′-hydroxy 4″-n-alkoxy benzoyloxy] azobenzenes and 4-n-hexyloxy-2′ hydroxy -4′-(4″-n-alkoxy benzoyloxy) azobenzenes, were synthesized by condensing equimolar quantities of 4-n-alkoxy-benzoyl chlorides with DA-1 and DA-2, respectively, in dry pyridine [17]. The mixture was allowed to stand overnight at room temperature. It was acidified with cold 1:1 aqueous hydrochloric acid. The solid obtained was separated and washed successively with saturated aqueous $NaHCO_3$ and water. The final product was recrystallized several times from acetic acid until constant transition temperatures were obtained. They are recorded in Table 1. The elemental analysis of all the compounds were found to be satisfactory and are recorded in Table 2. IR and ^{1}H NMR spectral data are given below.



SCHEME 1 Synthetic route to series I and II compounds.

TABLE 1 Transition Temperatures (°C) for Series I and II

R = n	Sc	N	I
Series I			
Methyl	–	137	250
Ethyl	–	108	255
Propyl	–	116	245
Butyl	–	138	250
Pentyl	–	127	230
Hexyl	–	101	235
Heptyl	–	105	230
Octyl	–	126	215
Decyl	101	125	197
Dodecyl	102	128	185
Tetradecyl	103	132	177
Hexadecyl	96	130	170
Series II			
Methyl	–	133	259
Ethyl	–	105	256
Propyl	–	119	242
Butyl	–	132	243
Pentyl	–	117	225
Hexyl	–	99	230
Heptyl	–	93	218
Octyl	–	108	220
Decyl	–	110	215
Dodecyl	93	116	210
Tetradecyl	90	120	200
Hexadecyl	86	122	190

FTIR (KBR) Spectra cm^{-1}

Series I ($nC_{12}H_{25}$): 3433 (-OH), 2920, 2800, 1732 (-COO-), 1604 (-N=N-), 1469, 1257, 1157, 1100, 1050, 1000, 850, 750, 700.

Series II (nC_2H_5): 3676, 3429 (-OH), 2923, 1728 (-COO-), 1604, (-N=N-), 1504, 1469, 1307, 1245, 1153, 1064, 975, 844, 750, 663.

Series II ($nC_{12}H_{25}$): 3568 (-OH), 2920, 2850, 1732 (-COO-), 1605 (-N=N-), 1508, 1469, 1399, 1249, 1168, 1006, 975, 884, 759, 690.

Proton NMR Spectra (Solvent $CDCl_3$) 90 MHz, δ ppm, Standard TMs)

Series I ($nC_{10}H_{21}$): δ 0.9–1.8 (m, 22H, 6H of 2 × CH_3 at C-1, C–4″ and 16 H of (8 × CH_2) at C–4″, 4.0 (t, 2H of -OCH_2 at C – 4″), 4.4 (q, 2H of

TABLE 2 Elemental Analysis of Series I and II Compounds

	% Calculated			% Found		
R = n-alkyl group	C	H	N	C	H	N
Series I						
Methyl	65.71	4.76	6.66	65.34	5.06	6.86
Ethyl	66.35	5.06	6.45	66.75	5.41	6.65
Propyl	66.96	5.35	6.25	66.77	5.48	6.08
Butyl	67.53	5.62	6.06	68.01	5.23	6.45
Pentyl	68.06	5.88	5.88	68.13	5.69	5.72
Hexyl	68.57	6.12	5.71	69.00	6.11	5.94
Heptyl	69.04	6.34	5.55	69.06	6.08	5.71
Octyl	69.49	6.56	5.40	69.19	6.06	5.88
Decyl	70.32	6.95	5.12	69.85	7.05	4.83
Dodecyl	71.08	7.31	4.87	70.78	7.41	4.53
Tetradecyl	71.76	7.64	4.65	71.87	7.96	4.29
Hexadecyl	72.38	7.93	4.44	71.97	8.22	3.99
Series II						
Methyl	69.74	6.25	6.25	70.17	6.34	5.88
Ethyl	70.12	6.49	6.06	70.60	6.23	6.44
Propyl	70.58	6.72	5.88	70.35	6.39	6.05
Butyl	71.02	6.93	5.71	70.83	6.65	5.25
Pentyl	71.42	7.14	5.55	71.00	6.77	6.00
Hexyl	71.81	7.33	5.40	72.37	7.49	5.35
Heptyl	72.18	7.51	5.26	72.59	7.61	5.40
Octyl	72.52	7.69	5.12	72.13	7.78	4.80
Decyl	73.17	8.01	4.87	73.51	7.80	5.26
Dodecyl	73.75	8.30	4.65	74.16	7.95	5.04
Tetradecyl	74.28	8.57	4.44	74.42	8.93	4.83
Hexadecyl	74.77	8.81	4.25	74.32	8.96	3.89

CH_2 of ester at C-1), 6.9 (m, 4H at C-3, C-5, C-3″, C -5″) 7.7 – 8.15 (m, 7H at C-2, C–6, C-3′, C–5′, C–6′ C–2″ and C–6″).

Series II (nC_5H_{11}): δ 0.9 (t, 6H, 2 × CH_3 at C-1 and C–4″), 1.2–1.8 (m, 14H, 7 × CH_2 at C–1 and C–4″) 4.0 (t, 4H, 2 × CH_2 of O–CH_2 at C–1 and C–4″), 7.0 (d, 6H at C–2, C–6, C–3″, C–5″, C–3 and C–5), 7.7–8.3 (m, 5H at C–6′, C–3′, C–5′, C–2″ and C–6″).

Calorimetry

Calorimetry is a valuable method for the detection of phase transition. Conclusions may be drawn concerning the nature of the phases that participate in the transition with the help of calorimetric studies. In the present study, enthalpies of dodecyl homologues of both the series

TABLE 3 DSC Data for Series I and II Compounds

Series	n	Transition	ΔH ($J\,g^{-1}$)	ΔS ($Jg^{-1}K^{-1}$)
I	12	Cr–Sm	36.316	0.0972
		Sm–N	0.1511	0.001293
		N–I	0.559	0.001262
II	12	Cr–Sm	45.671	0.1267
		Sm–N	0.736	0.00197
		N–I	1.919	0.00399

were measured by differential scanning calorimetry, and the data is recorded in Table 3.

RESULTS AND DISCUSSION

All the members of series I: 4-Carbethoxy – [2′-hydroxy 4′ – (4″-n-alkoxy benzoyloxy] azo benzenes and series II: 4-n-Hexyloxy – 2′-hydroxy – 4′-(-4″-n-alkoxy benzoyloxy)] azo benzenes exhibit enantiotropic nematic

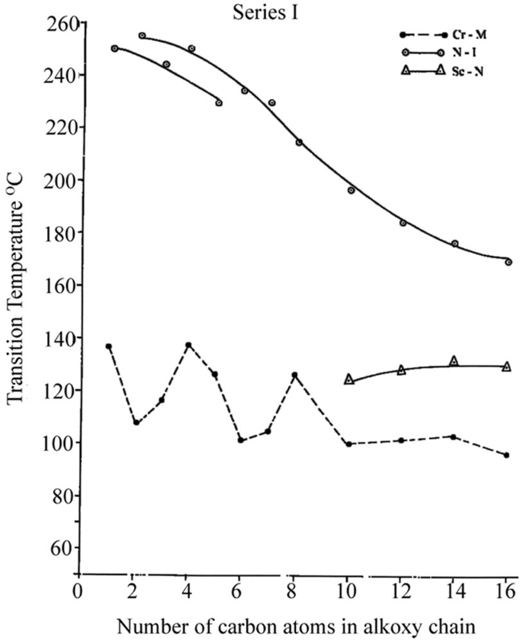


FIGURE 1 The phase behavior for series I.

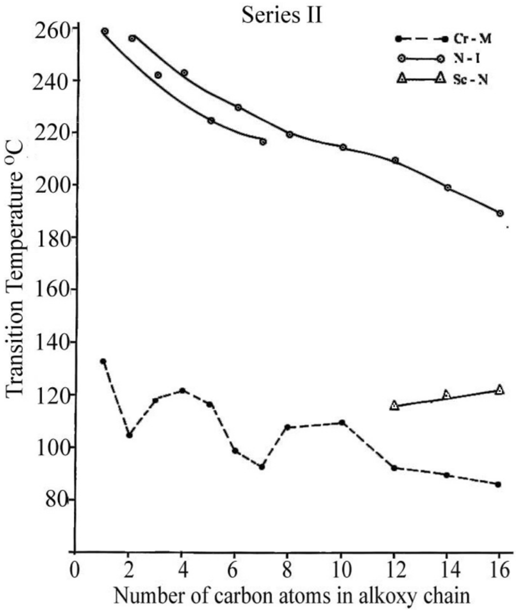
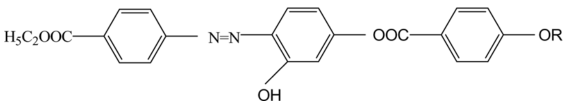


FIGURE 2 The phase behavior for series II.

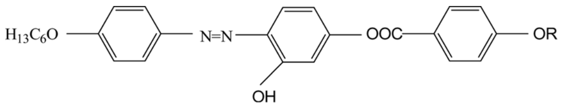
phases. The higher homologues exhibit smectic mesophases. The smectic phase persists up to the last member of the series. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figs. 1 and 2) shows a steady fall in nematic isotropic transition temperatures and exhibit odd and even effect.

Table 4 summarizes the average thermal stabilities and the comparative geometries of the present series I and II, and the structurally related series A [18], B [19], and C [20]. Table 4 shows that the nematic thermal stabilities of series I and II are almost the same. This indicates that the net effect imparted due to the end-to-end cohesive forces in both the series viz. series having carbethoxy group as well as the series having polarisable n-hexyloxy chain, is similar, as all the other molecular forces are the same.

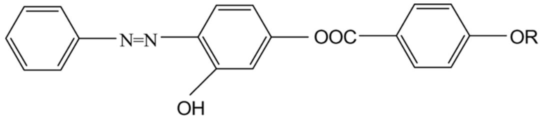
In Table 4, we have the following:



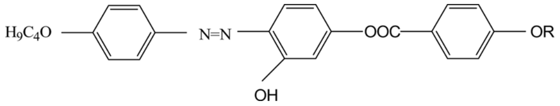
Series I



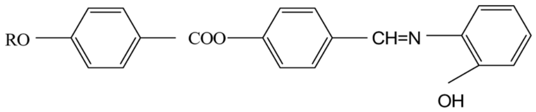
Series II



Series A



Series B



Series C

The smectic thermal stability of series I is a little higher (11^0C) than that of series II, which can be explained by the fact that the dipole moment of the terminal $-C_2H_5COO$- group in series I, operating along the long axis of molecules, contribute more to the lateral attractive forces of series I compared to the polarizable n-hexyloxy group, resulting in the higher smectic thermal stability of series I. An early appearance of the smectic phase in series I as compared to that in series II, can also be attributed to the increased polarity as explained above.

Table 4 further shows that the molecules of series I and series II are longer and more polarizable due to the presence of terminal groups at the both ends, whereas the molecules of series A have a terminal group at one end only. The length and polarizability are known to enhance mesogenic properties hence thermal stabilities of series I and series II should be higher than that of series A, which is the case.

Reference to the geometry of series II and series B show that they have similar structure except in their terminal substitutions. The Series II has n-hexyloxy group, whereas the series B has n-butoxy

TABLE 4 Comparative Geometry and Average Thermal Stabilities of Series I and II, A, B, and C

Transitions	I	II	A	B	C
Smectic to nematic or Isotropic (C_{12}–C_{16})	130	119.3	–	–	144.25
Nematic to isotropic (C_1–C_8)	238.75	236.62	150.8 (C_4 – C_8)	247.37	155.6
Commencement of smectic phase	C_{10}	C_{12}	–	–	C_4

group at that terminus. The nematic thermal stability of the series B is comparatively higher than that of series II. This may be due to the fact that in series II, the alkyl chain length is longer by two carbon atoms as compared to the series B. It is known [21] that increase of methylene spacer in alkoxy group decreases the end-to-end cohesive forces. This in turn results in lowering of nematic–isotropic transition temperatures. Therefore, series B exhibits higher N–I average thermal stability compared to series II.

The common aspects between series I, II, and C are that they all have three phenyl nuclei and an ester central linkage and a lateral phenolic (-OH) group. The lateral phenolic (-OH) group is on the central phenyl ring in series I and II, while it is on the terminal phenyl ring in series C. The difference between series I, II, and C is in the central linkage. Series I and II have an azo central linkage, whereas series C has an azomethine central linkage. Additionally, series I and II have terminal ester and n-alkoxy substituent, whereas series C has n-alkoxy substituent at one end only. The terminal group enhances length and overall polarizabilities of the molecules which results in higher nematic thermal stabilities of series I and II. This indicates that the shifting of –OH group on the terminal phenyl ring, ortho to Schiff base linkage, without n-alkoxy group at that end, lowers the nematic–isotropic thermal stabilities of the series C compared to the series I and II.

The average smectic thermal stability of the series C is higher than that of the series I and II, even though molecules of the series C are shorter in length than those of series I and II. The smectic phase also appears early in the series C. Vora and Gupta [20] have explained this behavior in the series C based on intramolecular hydrogen bonding with the schiff base linkage and the close packing of molecules in layers due to a gap arising from the overall geometry of the molecules.

ACKNOWLEDGMENT

The authors thank Dean Prof. B. S. Parekh, Dean, Faculty of Technology and Engineering, and Dr. C. N. Murthy, Head, Department of Applied Chemistry, for providing research facilities.

REFERENCES

[1] Ruslim, C., & Ichimura, K. (1998). *Chem. Lett.*, 789–790.

[2] Kozlovsky, M. V., Shibaev, V. P., Stakhanov, A. I., Weyrauch, T., & Iaase, W. I. (1998). *Liq. Cryst.*, *24*, 759.

[3] Shibaev, V. P., Kostomin, S. A., & Ivanov, S. A. (1996). In *Polymers as Electro-Optically and Photo-Optically Active Media*, V. P. Shibaev (Ed.), Springer: Berlin, 37.

[4] Ikeda, T., & Tsutsumi, O. (1995). *Science*, *268*, 1873.

[5] Anderle, K., & Wendorff, J. (1994). *Mol. Cryst. Liq. Cryst.*, *243*, 51.

[6] Hermann, D. S., Rudquist, P., Ichimura, K., Kudo, K., Komitov, L., & Lagerwall, S. T. (1997). *Phys. Rev. E.*, *55*, 2857.

[7] Asaki, T., Ikeda, T., & Ichimura, K. (1994). *J. Am. Chem. Soc.*, *116*, 625.

[8] Bauman, D. (1988). *Mol. Cryst. Liq. Cryst.*, *159*, 197.

[9] Schroeder, D. C., & Schroeder, J. P. (1974). *J. Am. Chem. Soc.*, *96*, 4347; Schroeder, D. C., & Schroeder, J. P. (1976). *J. Org. Chem.*, *41*, 2566.

[10] Vora, R. A., & Gupta, R. (1979). *Mol. Cryst., Liq. Cryst. Lett.*, *56*, 31; Vora, R. A., & Gupta, R. (1980). In Liquid Crystals, Chandrasekhar, S. (Ed.), Heyden Verlag: 589.

[11] Bayle, J. P., Berdague, P., Ho, M. S., & Fung, B. M. (1993). *Liq. Cryst.*, *14*, 667.

[12] Bayle, J. P., Perez, F., Berdague, P., Judeinstein, P., Allouchi, H., Chasseav, D., Cotrait, M., & Lapontaine, E. (1995). *Liq. Cryst.*, *19*, 345.

[13] Bayle, J. P., Perez, & Judeinstein, P. (1995). *New. J. Chem.*, *19*, 1015.

[14] Vyas, G. M., & Shah, N. N. (1963). *Org. Synth. Cl.* (Revised edition of annual Vol. 30–39) John Wiley and sons, Inc.: New York, Vol. VI, p. 836.

[15] Giswell, T. R., Klandermann, B. H., & Batesey, B. C. *Mol. Cryst. Liq. Cryst.*, *22*, 211.

[16] Vogel, A. I. (1989). Aromatic compounds: Aromatic amines, formation of dia azonium salts and their coupling reactions. In: *Text Book of Practical Organic Chemistry*, 5th Edn., ELBS, and Longmann Group, Ltd., p. 946.

[17] Dave, J. S., & Vora, R. A. (1970). In *Liquid Crystals and Ordered Fluids*, Johnson, J. F. & Porter, R. S. (Eds.) (Plenum Press), p. 477.

[18] Nandedkar, H. (1999). Ph.D. Thesis, Applied Chemistry Dept., M. S. University of Baroda.

[19] Kevat, J. B. (1998). Ph.D. Thesis, Applied Chemistry Dept., M. S. University of Baroda, Baroda.

[20] Vora, R. A., & Gupta, R. (1979). *Mol. Cryst. Liq. Cryst.*, *56*(7), 31.

[21] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystal*, Academic Press: London.