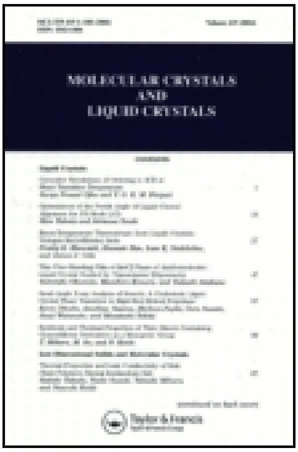

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Mesomorphic Behavior of Novel Liquid Crystalline: 2-[4′-n-Alkoxy Benzoyloxy]-Naphthylazo-2″-Methoxy Benzenes

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Version of record first published: 16 Nov 2012.

To cite this article: V. R. Patel , N. N. Vyas & A. V. Doshi (2012): Synthesis and Mesomorphic Behavior of Novel Liquid Crystalline: 2-[4′-n-Alkoxy Benzoyloxy]-Naphthylazo-2″-Methoxy Benzenes, Molecular Crystals and Liquid Crystals, 569:1, 15-23

To link to this article: http://dx.doi.org/10.1080/15421406.2012.693010

Mol. Cryst. Liq. Cryst., Vol. 569: pp. 15–23, 2012
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.693010

Synthesis and Mesomorphic Behavior of Novel Liquid Crystalline: 2-[4′-n-Alkoxy Benzoyloxy]-Naphthylazo-2″-Methoxy Benzenes

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Eleven members of a novel azoester homologous series entitled 2-[4′-n-alkoxy benzoyloxy]-naphthylazo-2″-methoxybenzenes are reported. The methyl to n-butyl homologues are nonmesomorphic, but the other homologues are mesomorphic. The pentyl, hexyl, and hexadecyl homologues exhibit only the nematic phase. The octyl, decyl, and dodecyl homologues exhibit a smectic phase in addition to the nematic phase, however, the tetradecyl homologue exhibits only a smectic phase. An odd–even effect with alternation of transition temperatures is observed for thenematic-isotropic transition curve. The average thermal stability and liquid crystal behavior for the smectic and nematicmesophases are 99.5° and 132.0°, respectively, and the mesomorphic properties are compared with structurally isomeric homologous series. Analytical data confirms the molecular structures of the novel materials. The textures from optical polarizing microscopy of the nematic and smectic phase show the expected Schlieren and focal conic appearances, respectively.

Keywords Azoester; Mesomorphism; mesophase; nematic; smectic

Introduction

A combination of molecular rigidity and flexibility, and anisotropic forces of attractions serve to dictate the occurrence of mesomorphism. The variation in molecular rigidity or flexibility is brought about by varying the terminal end groups on either side or the laterally substituted functional groups on the rigid core, which usually consists of phenyl rings. The present work concerns the evaluation and synthesis of a homologous series of azoesters with –OCH_3 as a laterally substituted functional group on the phenyl ring bridged through a –N=N- linkage in combination with n-alkoxy left terminal end group bridged through a –COO- central group as the flexible part of a molecule, and a naphthyl unit linked between two phenyl rings on either sides by central bridges, viz. –COO- and –N=N- as the rigid core of the molecule. Thus, the naphthyl moiety was selected to vary molecular rigidity, and the –OCH_3 lateral group and the n-alkoxy terminal groups were selected to vary molecular flexibility of the novel homologous series. This study will discuss the structural property

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Table 1. Elemental analysis for the hexyloxy and octyloxy derivatives

	Elemental% found (compared with% calculated)		
Molecular formula	C	H	N
$C_{30}H_{30}N_2O_4$	74.69 (74.70)	6.22 (6.29)	5.81 (5.75)
$C_{32}H_{34}N_2O_4$	75.29 (75.55)	6.66 (6.51)	5.49 (5.39)

relationships across the homologous series in terms of the molecular flexibility, molecular breadth, and polarizability on mesomorphic behavior.

Experimental

Characterization

Selected representative homologues of the series were characterized by infrared (IR), ^{1}H NMR, and elemental analysis. IR spectra were recorded on a Perkin Elmer spectrum GX, ^{1}H NMR spectra were recorded on Bruker spectrometer using $CDCl_3$ as a solvent, and microanalysis was performed on a Perkin Elmer PE 2400 CHN analyzer. Mesogenic properties were investigated using LeitzLaborlux 12 POL hot stage polarizing microscope (Ernst Leitz, Ltd., Midland, Ontario, Canada).

Synthesis

4-n-alkoxy benzoic acid and 4-n-alkoxy benzoyl chlorides (Z) were synthesized by a modified method of Dave and Vora [1]. 2-hydroxy-naphthyl azo–2′-methoxy benzene (Y) was prepared by known method of Furnis et al. [2]. 2-(4′-n-alkoxy benzoyloxy)-naphthyl azo-2”-methoxybenzenes were synthesized by condensing 4-n-alkoxy benzoyl chloride (Z) with 2-hydroxy-naphthyl-azo-2′-methoxybenzene (Y) in ice cold pyridine [3–5]. Azoester formed were filtered off, washed, and dried before crystallization. Crystallization continued until the final product gave constant transition temperatures. Analytical data confirms the molecular structures, as presented in Table 1. Ortho-anisidine, β-naphthol, sodium nitrate, pyridine, thionyl chloride, 4-hydroxy benzoic acid, n-alkyl halide, and other chemicals required for synthesis are used as received. The synthetic route to the present homologous series is outlined in Scheme 1.

Analytical Data

NMR in ppm. Decyl, 0.910 (alkyl group of $–OC_{10}H_{21}$), 1.27 (long $–CH_2$- chain), 1.656 ($-O-CH_2-CH_2$ of $–OC_9H_{21}$), 4.024 ($-O-CH_2-CH_2-$), 6.904 & 6.947 & 8.026 & 8.069 (p- sub. Benzene)

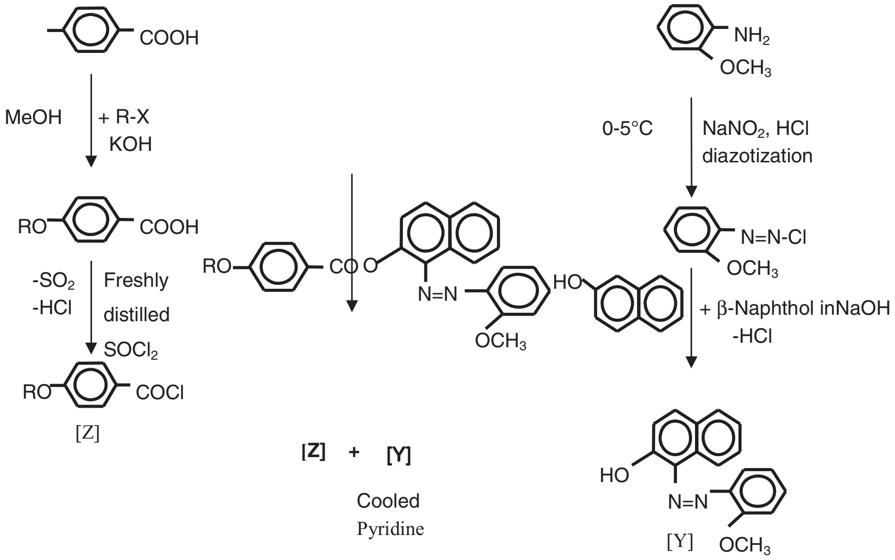
Dodecyl, 0.88 (alkyl group of $–OC_{12}H_{25}$), 1.26 (long –CH2- chain), 1.801.656 ($-O-CH_2-CH_2$ of $–OC_9H_{21}$), 4.024 ($-O-CH_2-CH_2-$), 6.904 & 6.947 & 8.026 & 8.069 (p-sub. Benzene)

IR in $\mathbf{Cm^{-1}}$. Hexyl, V_{max}/cm^{-1} 772 (o-sub. Benzene ring), 847 (p-sub. Benzene ring), 1024, 1108, 1678 (–COO- group), 1428 (-N=N- group), 2866 & 2939 (alkyl group), 1204 (-C-O of ether group)

Tetradecyl, V_{max}/cm^{-1} 748 (o-sub. Benzene ring), 844 (p-sub. Benzene ring), 1064, 1128 & 1716(–COO- group), 1431 (-N=N- group), 1107 cm^{-1} (-C-O of ether group), 719 (polymethylene of alkyl group), 694 & 748 (mono-sub. Benzene ring)

Texture:

Nematic	Texture
Hexyloxy	Threaded type
Octyloxy	Schlieren type
Smectic	
Dodecyloxy	Smectic A
Tetradecyloxy	Smectic C



where R = C_nH_{2n+1}, n = 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16.

Scheme 1. Structurally similar isomeric series.

Results and Discussion

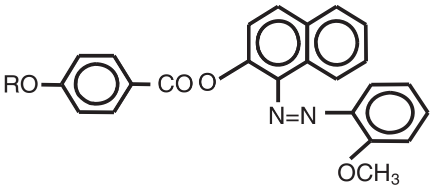
An azo dye 2-hydroxynaphthylazo 2′-methoxybenzene is not a liquid crystal but, on linking it with 4-n-alkoxybenzoyl chloride, the resultant majority of novel products are liquid crystalline, i.e., the pentyl to hexadecyl derivatives are monotropically or enantiotropically exhibited, as either smectic and/or nematic mesomorphism. The methyl to butyl homologues of the series are not liquid crystalline in character. A phase diagram (Fig. 1) of the novel series is drawn for the number of carbon atoms in the n-alkyl chain of the n-alkoxy terminal end group versus the transition temperatures of the series as recorded in Table 2, by joining related points. Solid-isotropic or solid-mesomorphic transition curve adopts a zigzag path of rising and falling values, and behaves in a normal manner. The transition curve initially rises,

Table 2. Transition temperatures in °C

Compound no.	n (for $R = \text{-}C_nH_{2n+1}$)	Smectic	Nematic	Isotropic
1	1	–	–	150.0
2	2	–	–	180.0
3	3	–	–	176.0
4	4	–	–	132.0
5	5	–	(155.0)	166.0
6	6	–	108.0	141.0
7	8	(86.0)	104.0	133.0
8	10	(107.0)	(125.0)	135.0
9	12	85.0	103.0	122.0
10	14	83.0	–	96.0
11	16	–	(101.0)	151.0

Note: Values in ( ) indicate monotropic.

Series 1: 2-[4'-n-alkoxy benzoyloxy]-naphthylazo-2"-methoxybenzenes.



smoothly passes through a maxima, and then gradually falls from the octyl to tetradecyl homologues without showing an odd-even effect. The curve is smoothly extrapolated to the hexadecyl derivative of the series to predict and to determine its latent transition temperature (LTT) for the probable occurrence of smectogenic mesophase formation. Thus, predicted LTT for smectic phase formation of hexadecyl derivative is 88.0°C. The nematic-isotropic transition curve shows a descending tendency as the series is ascended with the exhibition of an odd-even effect and alternation of transition temperatures, which appears from the pentyl to the nonyl derivatives. Both curves for the odd and even homologues merge into each other at nonyl to decyl derivatives, thus the nematic-isotropic curve behaves in the usual expected manner. The nematic mesophase exhibits a threaded or Schlieren texture and the smectic mesophase exhibits a focal conic fan-shaped texture of smectic A or smectic C, as determined by a miscibility method using optical polarizing microscopy. The nematic-isotropic transition temperatures are between 141.0°C and 122.0°C with the nematogenic range varying from a minimum of 19.0°C at the dodecyl homologue to a maximum of 33.0°C at the hexyl homologue, and the smectogenic phase range is between 13.0°C and 18.0°C for tetradecyl and dodecyl homologues, respectively. Thus, mesomorphic range of the smectic phase is shorter than that of the nematic phase. Hence, the series under discussion is predominantly nematogenic and partly smectogenic. The statement that liquid crystallinity involving a naphthyl unit of moderate chain length yields only or predominantly nematogenic character in the homologues [6,7] of the series is supported by the present investigation. The lack of mesomorphism of the methyl to butyl homologues is due to their high crystallizing tendency arising from the relatively high level of forces of attractions and the lack of flexibility to cause mesophase formation [6,8–10]. The exhibition of the smectic mesophase from the octyl to tetradecyl derivatives of the series is attributed to the presence of lamellar packing of the molecules caused by broadening of the nonlinear shape of molecules and laterally substituted highly polar methoxy group at ortho position to –N=N- central group, which increases molecular polarity and polarizability and raises suitable magnitude of anisotropic forces of attractions to cause sliding layered two-dimensional array of molecules. The exhibition of the nematic mesophase by the pentyl to hexadecyl homologues except tetradecyl homologue is attributed to the occurrence of molecular disalignment at an angle less than 90° with the plane of the surface under applied heat during floating condition which is due to the emergence of suitable magnitudes of anisotropic forces of intermolecular attractions related to molecular rigidity and flexibility [8–10] which resist exposed thermal vibrations, resulting to cause statistically parallel orientational order of molecules. Thus, the smectic phase in addition to the nematic phase or only the smectic or only the nematic mesophase appears, either monotropically or enantiotropically, for the homologous series under discussion. The alternation of transition temperatures and appearance of an odd-even effect in the nematic-isotropic transition is attributed to the progressively and sequentially added methylene unit in the n-alkyl chain of n-alkoxy flexible terminal end group. Such odd-even effect diminishes as the series is ascended because the longer n-alkyl chain may coil, bend, or flex in irregular manner. Thus, the nematic-isotropic transition curve follows a smooth trend from the longer chain lengths without any odd-even effect.

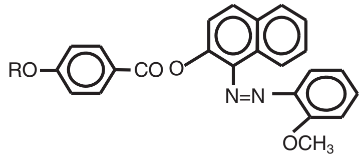
The liquid crystal properties of the titled homologous series 1 are compared with a structurally isomeric series X [3b] (Fig. 2) in terms of molecular characteristics and average thermal stabilities of the smectic and nematic mesophases which are shown in Table 3.

Both homologous series 1 and X are isomeric from point of view of their molecular formula, but they differ in their molecular arrangement. Series1 is polymesomorphic involving both the smectic and nematic mesophase; while series X under comparison gives rise to only nematic mesomorphism. The smectic-isotropic average thermal stability of series 1 is 99.5° while that of series X is zero. That is series X is nonsmectogenic. Likewise, the nematic-isotropic average thermal stability of series 1 is 132.0° while that of series X is 149.2°. Thus, nematic-isotropic thermal stability of series X is higher than series 1 of present series under discussion. Overall, mesophase length of series X is also higher than that of series 1. Hence, though series 1 shows lower phase length than series X, it exhibits both smectic and nematic types of mesophases while series X exhibits only the nematic

Table 3. Average thermal stability in °C

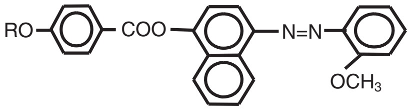
Series	1	X
Smectic–nematic or smectic-isotropic	(C_8–C_{14})	–
Commencement of smectic phase 99.5	C_8	–
Nematic-isotropic	132.0 (C_5–C_{12})	149.2 (C_6–C_{14})
Commencement of nematic phase	C_5	C_6

Series 1



2-[4'-n-alkoxy benzoyloxy]-naphthylazo-2"-methoxybenzenes

Series X



4-[4'-n-alkoxy benzoyloxy]-naphthylazo-2"-methoxybenzenes

Figure 1. Structurally similar isomeric series.

mesophase without exhibition of smectic mesophase. Both series 1 and X under comparison contain the same two phenyl rings in addition to a naphthyl unit at the center, the same central groups [viz., –COO- and –N=N-] and same n-alkoxy terminal end group as well as laterally ortho substituted –OCH$_3$ group at the same identical position. Thus, molecules of series 1 and X are identical with respect to their rigid part, flexible parts in addition to molecular aromaticity but, they differ in geometrical shape, size, molecular length, magnitude of breadth, length to breadth ratio, ratio of the polarity to polarizability, and many other parameters which have direct relation with suitable magnitudes of anisotropic forces of intermolecular attractions required for emergence of smectic and/or nematic mesophase or mesophase formation under the influence of applied heat from surrounding to a thermodynamic system. Such above molecular variations causes difference in mesomorphic properties from series to series for the same homologue and homologue to homologue

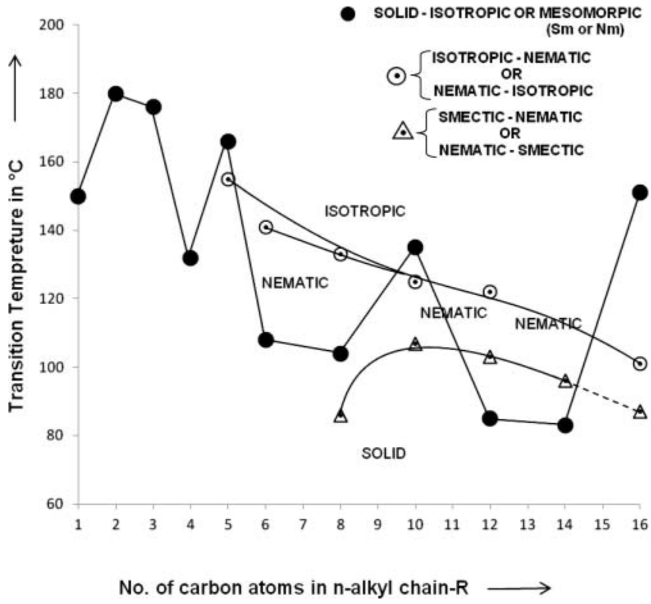


Figure 2. Structurally similar isomeric series.

in the same series. Geometrically, the arrangement of atoms in space of the molecules of series 1 and X appreciably differs in respect of the extent of their molecular width. Therefore, net molecular polarity and polarizability vary according to molecular width and length to breadth ratio. Greater molecular width (i) increase intermolecular distance and reduces the magnitude of intermolecular anisotropic forces of attractions on one hand, while on the other hand, (ii) increases the magnitude of intermolecular anisotropic forces of attractions due to increased molecular breadth or polarizability. Thus, two opposing effects, viz., (i) and (ii) are operating at a time. Therefore, net resultant effect observed is, that of predominating effect out of two opposing effects (i) and (ii) operating at a time. In case of lower value of average nematic-isotropic thermal stability or total mesophase length of series 1 as compared to series X is attributed to the predominancy of factor (i), which resists the thermal vibrations to cause statistically parallel orientational order of molecules in floating condition a little bit less in series 1 as compared to series X. The absence of smectogenic character in series X and appearance of smectogenic character in addition to nematic mesophase in series 1 is attributed to the absence and presence of lamellar packing in the crystal lattices, respectively, depending upon net result effect, out of two opposing effects (i) and (ii). The commencement of smectic phase occurance from octyloxyhomologue in series 1, which does not occur until the last hexadecyl homologue in series X. This observation is attributed to the extent of noncoplanarity caused by the molecule due to electron–electron interactions and steric interactions [3,6]. This effect, i.e., difference in magnitude of noncoplanarity of molecule of series 1 and series X is responsible to cause early or late commencement of smectic phase. Thus, lamellar packing in crystal lattices of molecules of series 1 is possible while it lacks in case of molecules of series X. Hence, smectogenic character in series X is absent till the last hexadecyl derivative and it appears from the octyloxy homologue of series 1. The stable state of a substance is associated with definite quantity of energy stored by the molecule at room temperature and one atmospheric pressure. That is, thermodynamically it is called enthalpy change (H) of a substance at normal temperature and pressure. As heat is supplied to a sample substance (system) from a surrounding to system; supplied heat energy from surroundings operates against the intermolecular anisotropic forces of attractions and molecules tend from stabilized state to destabilized state at a temperature T_1. Under this condition, molecules of a sample substance under investigation are disaligned at an angle less than 90° with the plane of a surface resisting exposed thermal vibrations and acquire mesophase formation at T_1. Mesophase formation continues till a higher temperature T_2 and then mesophase disappears for anisotropic liquid crystal. As temperature rises beyond T_2, molecules are randomly oriented in all possible directions in an irregular manner, such randomness or molecular disorder or entropy increases with a rise of temperature and decreases with a fall of temperature. Similarly, for monotropic liquid crystal $T_2 < T_1$, where T_1 is isotropic temperature or higher temperature. Difference of T_1 and T_2 is called a phase length or a range of liquid crystallinity. Thus, S value is calculated for any transition state from DSC scans using H value of corresponding transition temperature value. Thus, thermal stability values are related with a H value of a sample substance. The variation in mesomorphic properties from homologue to homologue in the same series and from series to series for the same homologue are due to the sequentially added methylene unit and laterally or terminally present functional group of fixed polarity, respectively. Thus, according to Gray's view [3,6] that, presence of anaphthyl unit in a molecular moiety induces nematogenic character relatively more and increase in molecular breadth reduces smectogenic character and smectic–nematic thermal stability. This statement is well supported by present investigation. Hence, the smectic and nematic group efficiency order derived on the bases of thermal stability are as under with reference to $–OCH_3$ laterally substituted group, which widens or broadens the molecular shape.

Nematic group efficiency order for lateral $–OCH_3$	Series X (Semi linear)	>	Series 1 (Nonlinear)
Smectogenic group efficiency order for lateral $–OCH_3$	Series 1 (Nonlinear)	>	Series X (Semi linear)

Conclusion

The presence of a naphthyl unit in a mesogenic molecule restricts or hinders lamellar packing of the molecules in their crystal lattices. However, broadening of a molecule favors to induce smectic character.

A naphthyl moiety reduces thermal stabilities of mesophase.

Homologous series involving a naphthyl unit are only nematogenic or predominantly nematogenic.

The degree of widening of a molecule containing anaphthyl unit is effective to induce only nematogenic character or smectogenic character in addition to nematogenic character in isomeric homologous series.

Radiation in molecular rigidity and flexibility plays an important vital role in liquid crystal behavior.

Thus, present investigation support the early views [1,4–5,11] and raises the credibility to the conclusion drown in past.

Acknowledgments

The authors are thankful to the management of S.P.T. Arts and Science College–Godhra and M.V.M. Science and Home Science College–Rajkot for their valuable support in the present investigation. Also, we thank the CSMCRI–Bhavnagar for their analytical services.

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