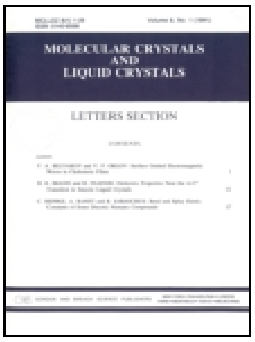


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Mesomorphism of azo-esters and chalcone-esters

B. B. Jain, Vinay S. Sharma, H. N. Chauhan & R. B. Patel

To cite this article: B. B. Jain, Vinay S. Sharma, H. N. Chauhan & R. B. Patel (2016) Mesomorphism of azo-esters and chalcone-esters, Molecular Crystals and Liquid Crystals, 630:1, 102-111, DOI: 10.1080/15421406.2016.1146910

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1146910

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 630, 102–111
http://dx.doi.org/10.1080/15421406.2016.1146910

Mesomorphism of azo-esters and chalcone-esters

B. B. Jain, Vinay S. Sharma, H. N. Chauhan, and R. B. Patel

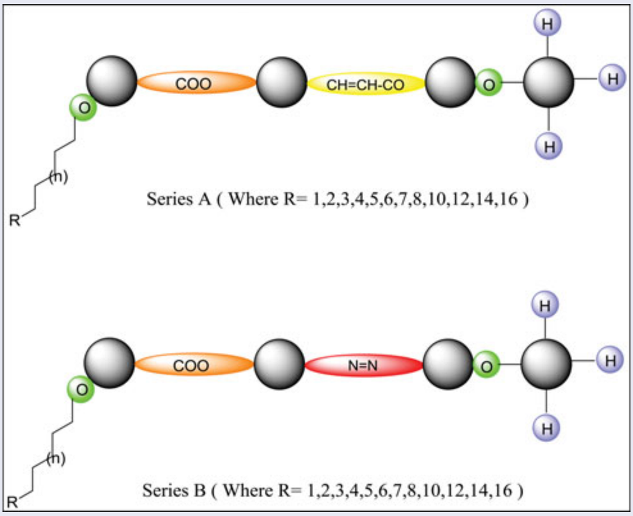
Chemistry Department, K. K. Shah JarodwalaManinagar Science College, Gujarat University, Ahmedabad, Gujarat, India

ABSTRACT

One chalcone-ester homologous series of mesogens α-4-[4$^{/}$-n-alkoxybenzoyloxy phenyl β-4$^{//}$methoxy benzoyl ethylenes (A) and one azo-ester homologous series of mesogens p-(p$^{/}$-n-alkoxybenzoyloxy) phenyl azo-p$^{//}$-methoxy benzene (B) being structurally similar are discussed. Both series (A) and (B) differ in respect of central bridges linking two phenyl rings. Mesomorphic properties start from 6th and 1st member of series (A) and (B) respectively. In series (A), 6th to 12th members show both smectogenic and nematogenic properties, and the 14th and 16th members show only nematogenic property. While in series (B), 1st to 10th members show nematogenic properties, 11th member shows both smectogenic and nematogenic properties, while 12th member shows only smectogenic property. Thermal stability of series (A) is relatively high as compared to series (B). Transition temperatures are observed through hot stage polarizing microscope by the miscibility method. Analytical data support the structure of molecules. Textures of series (A) in nematic are threaded and Schlieren in SmecticSmectic A type, while that of series (B) in nematic are threaded in SmecticSmectic A and smectic C.

KEYWORDS
Azo-ester; chalcone-ester; mesogen; mesophase; nematic; smectic

GRAPHICAL ABSTRACT



CONTACT B. B. Jain ✉ bijendrajain1988@gmail.com K. K. Shah JarodwalaManinagar Science College, Gujarat University, Ahmedabad-380008, Gujarat,India.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

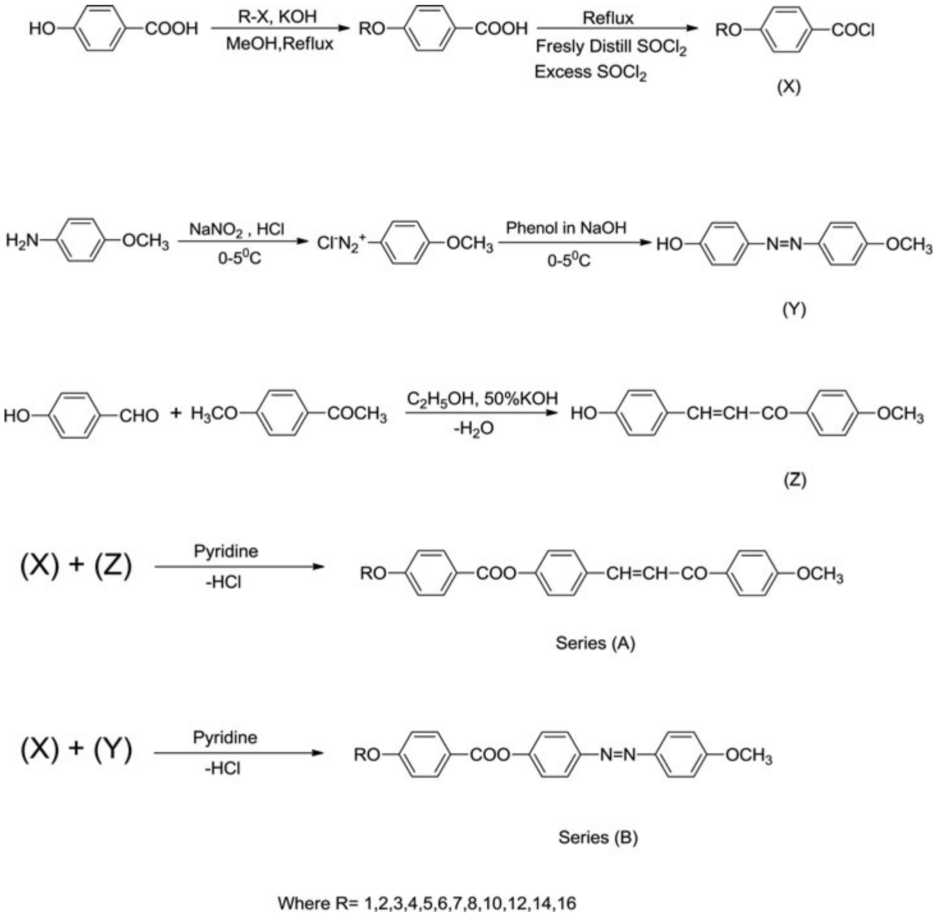
Introduction

The relation between mesomorphic property and molecular structure has been established with reference to varying terminally and or laterally substituted functional groups of molecules, but less attention has been given to central bridges linking phenyl rings [1–6]. Therefore, present investigation is planned with a view to establish the effect of central bridge on mesomorphic behavior of molecules [7–14]. The number of liquid crystal compounds consisted of rigid part as two or three phenyl rings bridged through central bridge and flexible part as varying left polar terminal, alkyl, or alkoxy end group keeping right terminal end group intact of fix polarity with or without lateral substitution [15–18].

Experimental

Synthesis: Series A

4-Hydroxy benzoic acid is alkylated by using suitable alkylating agents and resulting n-alkoxy benzoic acid is converted into n-alkoxy benzoyl chloride (X) by using thionyl chloride by the Dave and Vora method. α-4-Hydroxy phenyl β-4$'$methoxy benzoyl ethylene (Z) was prepared by reacting p-hydroxyl benzaldehyde and p-methoxy acetophenone by the established method. Compounds (X) and (Z) condensed in cold dry pyridine by the known method.



Scheme 1. Synthesis route of series (A) and (B).

The final product was decomposed, filtered, washed, dried, and recrystallized until a constant temperature is not obtained.

Series B

4-Hydroxy benzoic acid is alkylated by using suitable alkylating agents, and the resulting n-alkoxy benzoic acid is converted into n-alkoxy benzoyl chloride (X) by using thionyl chloride by the Dave and Vora method. 4-((4-Methoxy phenyl)diazenyl) phenol was prepared by diazotized 4-metoxyaniline and coupling of diazonium salt with phenol in basic condition. Compounds (X) and (Y) were condensed in cold dry pyridine by the known method. The final product was decomposed, filtered, washed, dried, and recrystallized until constant temperature is not obtained.

Characterization

Representative homologues of a series were characterized by infrared (IR) spectroscopy, and ^{1}H NMR spectra. IR spectra were recorded by Perkin–Elmer spectrum GX,[1] and H NMR spectra were recorded on Bruker using $CDCl_3$ as a solvent. Transition temperature and LC properties (textures) were determined using an optical polarizing microscopy equipped with heating stage. Textures of nematic phase were determined by the miscibility method.

Spectral data

For series (A)

IR in cm^{-1}

Hexyloxy

720 (-$(CH_2)_n$ of $-OC_6H_{13}$), 815 (phenyl ring), 1175 (C–O of $-OC_6H_{13}$), 1215, 1260, and 1640 (–COO), 930 (–CH=CH–).

Decyloxy

760 (–$(CH_2)_n$of $-OC_{10}H_{21}$), 830 (phenyl ring), 1175, 1150 (C–O of $-OC_{10}H_{21}$), 1250, 1610, and 1680 (–COO–), 945 (–CH=CH–).

NMR in ppm

Octyloxy

0.983 ($-CH_3$ of $-OC_8H_{17}$), 1.422 (–(CH_2)n of $-OC_8H_{17}$), 3.675 ($-OCH_2$ of $-OC_8H_{17}$), 6.565 and 6.582 (–CH=CH–CO), 7.404, 7.093, and 7.636 (phenyl ring).

Dodecyloxy

0.945 ($-CH_3$ of $-OC_8H_{17}$), 1.465 (–(CH_2)n of $-OC_8H_{17}$), 3.689 ($-OCH_2$ of $-OC_8H_{17}$), 6.575 and 6.669 (–CH=CH–CO), 6.691, 7.610, and 7.632 (phenyl ring).

Texture Determination

Tetradecyl–nematic–threaded
Decyl–smectic–smectic-A type
Hexyl–smectic–smectic-A type
Octyl–nematic–Schlieren

For series (B)

IR in cm^{-1}

Butoxy

2291, 2848 confirm alkyl group
1729 confirm >C=O ester
1495, 1463, 1579, 1605 confirm aromatic phenyl ring
1320 Confirm –N=N-
1257, 1169 confirm C–O ether linkage
844 confirm P- substituted phenyl ring

Octyloxy

2940, 2856 confirm alkyl group
1735 confirm >C=O ester
1500, 1471, 1582, 1610 confirm aromatic phenyl ring
1322 confirm -N=N-
1257, 1069 confirm –C–O ether linkage
849 confirm P-substituted phenyl ring

Texture determination

Tetradecyl–smectic–smectic-A type
Hexadecyl–smectic–smectic-C type
Butoxy–nematic–threaded
Octyloxy–nematic–threaded

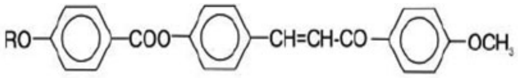
Result and discussion

n-Alkoxy benzoic acids are dimeric through hydrogen bonding. Dimerization disappears as a result of breaking of hydrogen bonding on esterification by α-4-hydroxy phenyl β-4$^{/}$methoxy benzoyl ethylene and 4-((4-methoxy phenyl)diazenyl) phenol, thus transition temperatures of homologous series (A) and (B) are relatively lower than the corresponding n-alkoxy acids from which the final products are obtained. α-4-hydroxy phenyl β-4$^{/}$methoxy benzoyl ethylene and 4-((4-methoxy phenyl)diazenyl) phenol are non-mesomorphic but on linking with n-alkoxy phenyl ring through central linkage exihibit mesomorphic characteristics. In series (A), methyl to pentyl derivatives of the series are non-mesogenic, but all others are mesogenic. The hexyl to dodecyl derivatives are enantiotropically smectogenic and nemactogenic in character. The tetradecyl and hexadecyl derivatives of the series are only enantiotropically nematogenic without exhibition of a smectic phase. In series (B), the nematic phase of mesophase commences from the very first number of the series, polymesomorphism is exhibited by tetradecyl homologue, i.e. smectic and nemactic mesophases appear one after the other. Hexadecyl number is purely smectogenic.

Transition temperatures of homologous series given in Table 1 are plotted against the number of carbon atoms in the n-alkyl chain of left n-alkoxy terminal. Smooth curves are drawn through similar or related points, the phase diagrams obtained are shown separately in Figs. 1 and 2. In Fig. 1, the solid isotropic or mesomorphic transition curve rises and falls as the series

Table 1. Transition temperature of series (A) and (B).

		Transition temperatures (°C)					
		Smectic Series		Nematic Series		Isotropic Series	
Sr. No.	n-alkyl group	(A)	(B)	(A)	(B)	(A)	(B)
1.	Methyl	—	—	—	165.0	164.0	335.0
2.	Ethyl	—	—	—	169.0	151.0	326.0
3.	Propyl	—	—	—	103.0	169.0	173.0
4.	Butyl	—	—	—	120.0	148.0	302.0
5.	Pentyl	—	—	—	108.0	152.0	262.0
6.	Hexyl	125.0	—	133.0	128.0	171.0	265.0
7.	Heptyl	113.0	—	135.0	120.0	172.0	252.0
8.	Octyl	112.0	—	139.0	122.0	174.0	242.0
10.	Decyl	110.0	—	131.5	121.0	164.0	219.0
12.	Dodecyl	110.0	—	129.0	125.0	157.0	202.0
14.	Tetradecyl	—	116.0	126.0	136.0	148.0	191.0
16.	Hexadecyl	—	112.0	128.0	—	135.0	138.0



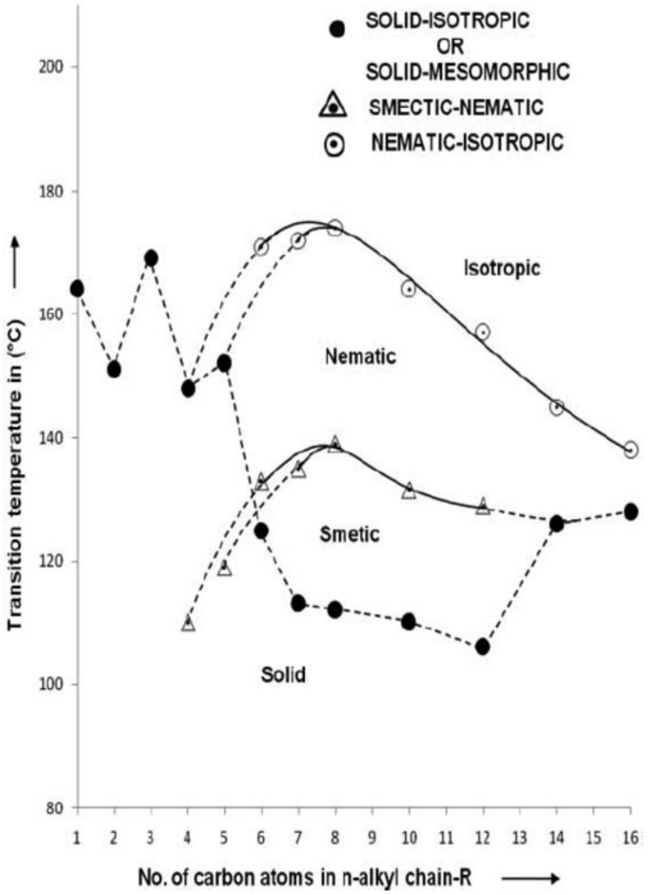


Figure 1. Phase behavior of series (A).

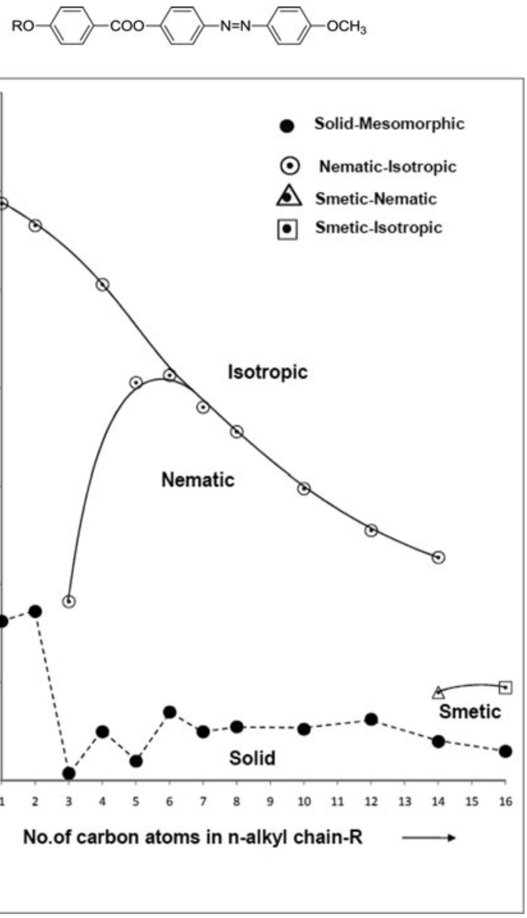
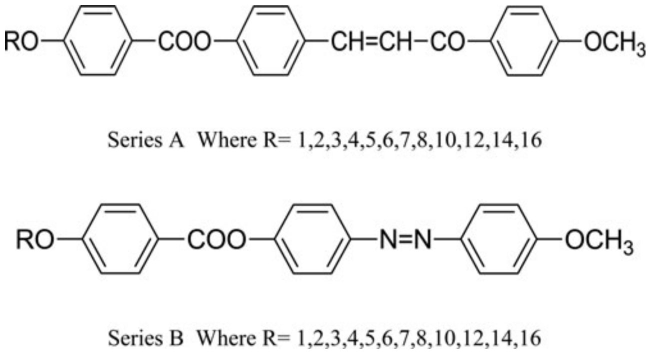


Figure 2. Phase behavior of series (B).

is ascended with an overall falling nature. The smectic–nematic transition curve initially rises, passes through maxima, and falls in a usual manner up to decyloxy homologues, but it rises by 1^0n in dodecyl derivative. The nematic–isotropic transition curve rises initially and then adopts a descending tendency as the series is ascended and behaves in a usual manner with an odd-even effect. In Fig. 2, the nematic–isotropic transition curve shows a smooth descending tendency as series is ascended. The solid mesomorphic curve follows a zig-zag path of rising and falling nature. In the case of first and seventh member of the series, it shows rise and fall of solid nematic transition temperature from and beyond the seventh homologue of this series, the solid mesomorphic curves show an overall falling tendency with negligible rise at the eighth and twelfth homologue. Nematic–isotropic transition curve behaves in a normal manner.

In series (A), non-mesogenic behavior of the first five homologues is attributed to their high crystallizing tendency arising from their amount of energy released to stabilize in crystalline solid state at room temperature. These non-mesogenic molecules are unable to resist thermal vibration and pass directly into isotropic liquid without passing through any mesogenic state, and rest of the homologues are capable to resist thermal vibration and consequently exhibit nematic and smectic phases. In series (B), mesogenic behavior started from the first homologue.

The structurally similar homologous series (A) and (B) [19,20] are as under:



Series A Where R= 1,2,3,4,5,6,7,8,10,12,14,16

Series B Where R= 1,2,3,4,5,6,7,8,10,12,14,16

Scheme 2. Series A and B.

In Figs. 3 and 4, we represent the 3D diagrams of series A and B having different central linkage groups and present and exhibit different mesogenic properties. The mesomorphic properties of a substance depend upon polarity, polarizability, aromaticity, linearity, length-to-breadth ratio, geometrical shape and size, π electron density, and many other factors of molecules that contribute to the net intermolecular forces of attraction, and hence to the mesomorphic properties and the degree of mesomorphism.

In Fig. 4, it is clear that geometrical shape of the molecules is linear rod-like without lateral substitution. Both molecules consist of left alkoxy terminal, three phenyl rings, and $-OCH_3$ right terminal. They differ only with respect to central bridges for the same homologue from series to series. Molecule of homologous series (A) links three phenyl rings through –COO (ester) and –CH=CH-CO (chalcone) central bridge, while that of homologous series (B) links three phenyl rings through –COO (ester) and N=N (azo) central bridge. Thus, aromaticity due to three phenyl rings of molecules,

The transition temperature of homologous series (A), which is relatively lower than the transition temperature of homologous series (B), is compared for the same homologues from series to series. This difference in transition temperature can be directly linked to

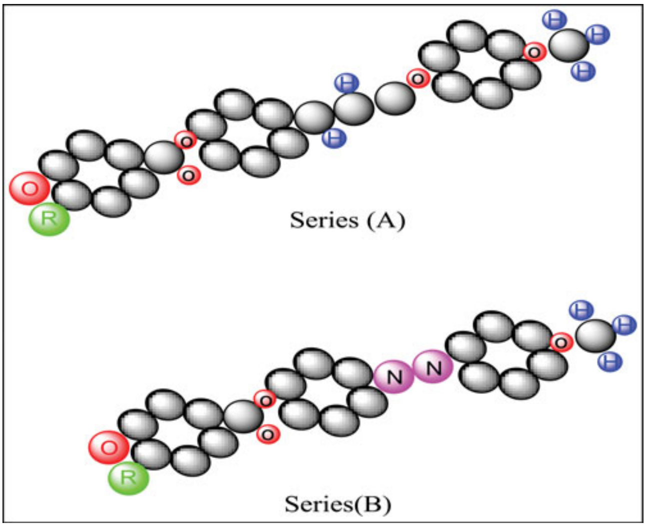


Figure 3. 3D diagram of series (A) and (B) (where R = side chain).

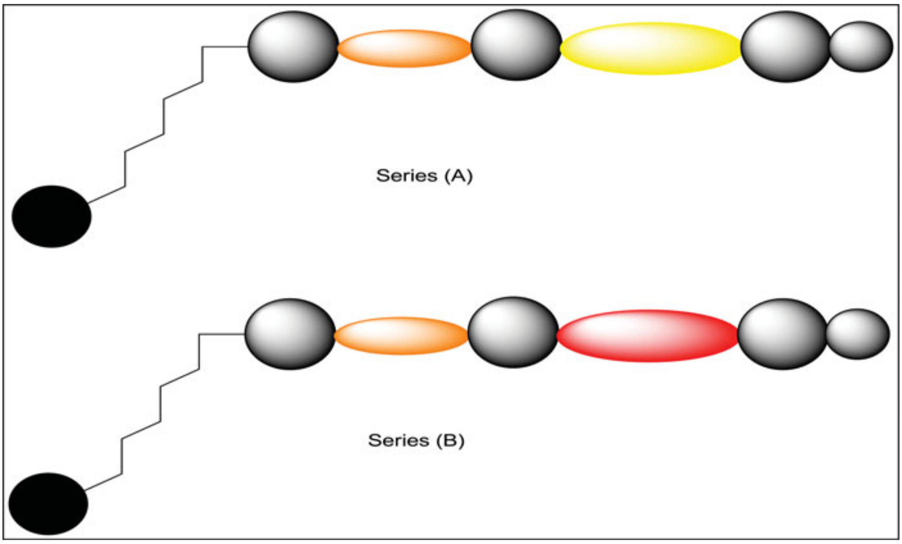


Figure 4. Space filling diagram of series (A) and (B).

the difference in intermolecular forces of attraction caused by the difference in length by –CH=CH-CO, N=N, and length-to-breadth ratio, resulting into difference in polarity and polarizability of molecules. It is observed that the overall phase length or degree of mesomorphism (for smectic) by series (A) is more than series (B), while the overall phase length or degree of mesomorphism (for nematic) by series (B) is more than series (A). Thus, two-dimensional array of molecules even in the floating condition maintains more statistically parallel orientational order, resisting thermal vibrations in series (A) than in series (B). Average thermal stability for smectic and nematic mesophase for homologous series (A) is more than that for homologous series (B).

On comparing the type of mesomorphic phase exhibited by homologous series (A) and (B) with series (Z), i.e. α–4–[$4^{/}$-n-alkoxycinnamoyloxy] phenyl β-4”-methoxy benzoyl ethylenes, its structure is given below:

Series C (where R = 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16)

Series C (Figure 5) is entirely nematogenic without exhibition of any smectogenic characteristic. Thus, series (C) is smectogenic, while both series (A) and (B) are smectogenic and nematogenic. Hence, the same central bridge and terminal groups bearing –CH=CH-COO, and -CH=CH-CO (series C) are nematogenic, and the same central and terminal groups bearing -COO-, -CH=CH-CO, and –COO-, -N=N- (series A and B) are both smectogenic and nematogenic. Thus, -COO- group can induce smectic character favorably more, and -CH=CH-COO- group can induce nematogenic character favorably more. Hence, -CH=CH-COO- is strong enough to emerge nematic character from smectic character and vice versa. Thus, group efficiency orders derived for induction of smectic and/or nematic characters are as under:

Smectic character group efficiency order:

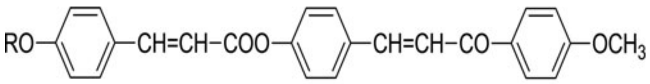
-COO > -CH=CH-COO

-CH=CH-C0 > N=N

Nematic character group efficiency order:

-CH=CH-COO > -COO

-N=N > -CH=CH-CO



Series C (Where R= 1,2,3,4,5,6,7,8,10,12,14,16)

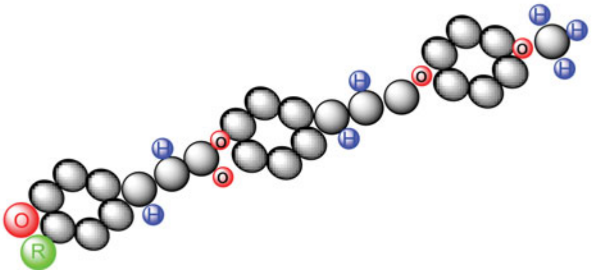


Figure 5. 3D Diagram of series (C) (where R = side chain)

Conclusions

In summary, we have examined that ester homologous series are not necessarily smectogenic but it may be entirely smectogenic or entirely nematogenic or partly smectogenic and partly nematogenic. We should compare the effect of ester linkage group in series (A) linked with the chalcone linkage group and the ester linkage group in series (B) at linked with the azo linkage group. We were able to compare mesomorphism property of series (A) and (B) with series (C), which determined the effect of vinyl ester at one end.

Acknowledgment

Authors acknowledge thanks to Dr. R.R. Shah, principal of K.K. Shah JarodwalaManinagar Science College, Ahmedabad.

References

[1] R. Walter. Ber. Disch. Chem. Ges. 1925 B58. 2302.
[2] Dave, J. S., & Vora, R. A. (1970). In: *Liquid Crystals and Ordered Fluids*, J. F. Johnson & R. S. Porter (Eds.), Plenum Press: New York, NY, 447 pp.
[3] Doshi, A. V., & Lohar, J. M. (1973). *J. Inst. Chemists (India)*, 65, 15–17.
[4] Dave, J. S., & Vora, R. A. (1974). *Mol. Cryst. Liq. Cryst.*, 28, 209.
[5] (a) Gray, G. W. (1962). *Molecular Structure and the Properties of Liquid Crystal*, Academic Press: London. (b) Gray, G. W., &Windsor, P. A. (1974). *Liq. Cryst. Plastic Cryst.*, Vol. 1.1, Chap. 4, Ellis Harwood: Chichester, UK.
[6] Dave, J. S., & Kurian, G. (1977). *Mol. Cryst. Liq. Cryst.*, 42, 175.
[7] Vogel, A. I. (1989). *Textbook of Practical Organic Chemistry*, 5th ed., ELBS and Longmann: London, 946 pp.
[8] Hird, M., Toyne, K. J., & Gray, G. W. (1993). *Liq. Cryst.*, *14*, 741.
[9] Chauhan, M. L., & Doshi, A. V. (2007). *J. Indian Chem. Soc.*, *84*, 774.
[10] Patel, V. R., & Doshi, A. V. (2010). *Der Pharma Chemica*, *2*, 429.
[11] Patel, R. B., & Doshi, A. V. (2011). *Der Pharma Chemica*, *3*, 147.

[12] (a) Chauhan, M. L., Pandya, R. N., & Doshi, A. V. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 228. (b) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, 548, 220. (c) Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 3. (d) Doshi, A. V., Odedara, D. A., & Patel, R. B. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 97. (e) Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104.

[13] Sharma, V. S., Solanki, R. B., Patel, P. K., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, *625*, 137–145.

[14] Doshi, A. V., & Makwana, N. G. (2008). *J. Ind. Chem. Soc.*, *85*, 263–266, 257–261.

[15] Chauhan, H. N. & Doshi, A. V. (2012). *Der Pharma Chemica*, 4(2), 731–736.

[16] Suthar, D. M., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *569*, 64.

[17] Chaudhari, R. P., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 569, 49.

[18] Chauhan, B. C., Shah, R. R. & Doshi, A. V. (2011). *Der Pharma Chemica*, 3(2), 110–117.

[19] Bhoya, U. C. & Doshi, A. V. (2011). *Der Pharma Chemica*, 3(2), 135–141.

[20] Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 570, 12–19.