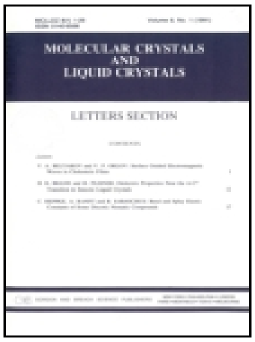
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Study of mesomorphism and its relation to molecular structure with special reference to central bridges viz. –COO– and –CH=CH–COO– of the homologous series

V. S. Sharma, R. B. Solanki, P. K. Patel, and R. B. Patel

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

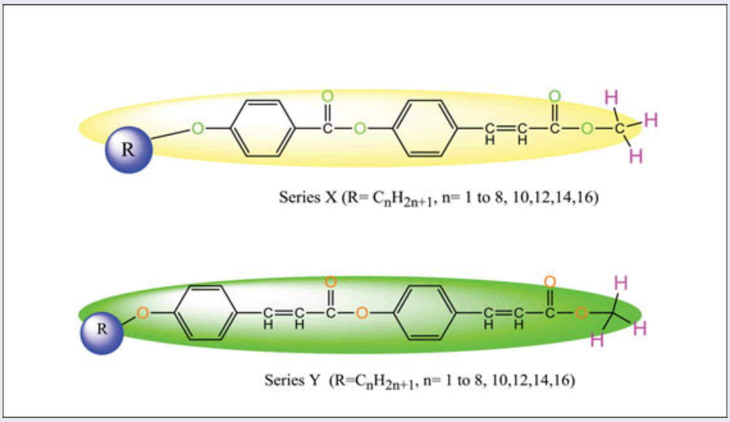
ABSTRACT

Two ester homologous series of mesogens, viz., Methyl-p-(p′-n-alkoxy benzoyloxy) cinnamates (X) and Methyl-p-(p′-n-alkoxy cinnamoyloxy) cinnamates (Y) being structurally similar are discussed. Both (X) and (Y) differ in respect of central bridges linking two phenyl rings. Only enantiotropic nematogenic character is observed without exhibition of any smectic character by all members of series (X) and (Y). Thermal stability of series (X) is relatively low as compared to (Y), but nematogenic mesophase lengths are of reverse order. Solid-nematic/solid-isotropic and nematic-isotropic transition curves in the phase diagrams behave in normal manner.

KEYWORDS

Mesogen; mesophase; nematic; smectic

GRAPHICAL ABSTRACT



Introduction

The relation between mesomorphism 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. Therefore, the present

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CONTACT V. S. Sharma vinaysharma3836@gmail.com Chemistry Department, K. K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad 38008, Gujarat, India.

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investigation is planned with a view establishing the effect of central bridge on mesomorphic behavior of molecules. The novel liquid crystal compounds consist 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.

Experimental

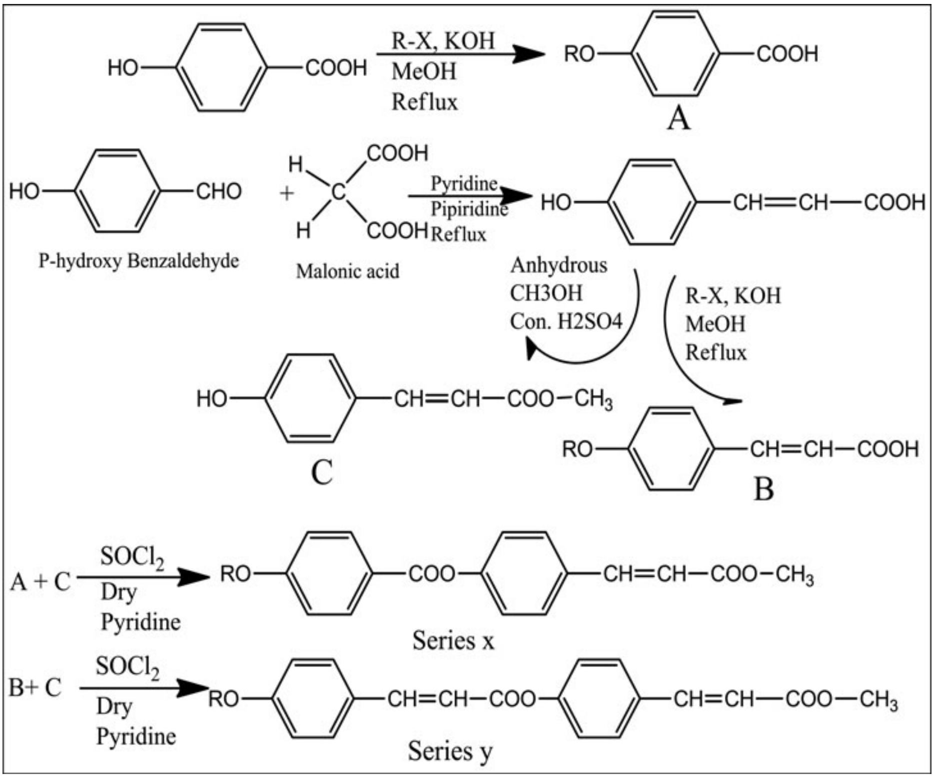
(i) n-Alkoxy (benzoic and cinnamic) acids: p-n-alkoxy benzoic acids and p-n-alkoxy cinnamic acids were prepared by usual established methods[1–5] by reaction of p-hydroxy acids and the corresponding alkyl halide (Scheme 1).

(ii) p-n-Alkoxy acids were converted to the acid chlorides by refluxing with freshly distilled thionyl chloride until the evolution of SO_2 ceases and then the excess of thionyl chloride was distilled off [6].

(iii) Acid chlorides were carefully treated with a pre-cooled solution of p-hydroxy methyl cinnamate dissolved in pyridine. Final products were obtained and subsequently dried, purified, and crystalized from alcohol.

(iv) The methyl ester of cinnamic acid was prepared by a usual established method [7–10] m.p. 117.0 °C, yield is 69.6%.

The transition temperatures of the homologs were determined by hot stage polarizing microscope. Infra-red (IR) and nuclear magnetic resonance (NMR) spectra of representative homologs of the series under comparison confirm the structure of the molecules. Analytical data support the structure.



Scheme 1. Preparation of series X and series Y ($R = C_nH_{2n+1}$).

Spectral Data for Series-X: NMR in ppm

Octyl.

0.890—CH_3 of C_8H_{17}, 1.308—CH_2 of C_8H_{17}, 1.772—OCH_2–CH_2 of –C_8H_{17}, 3.816—O–CH_3, 4.021—OCH_2– of O–C_8H_{17}, 6.380 and 6.460—CH=CH–, 6.905 and 8.026—P-Sub. Phenyl ring, 7.260—another P-Sub. Phenyl ring.

NMR confirms the structure.

Decyl.

0.880—CH_3 of $C_{10}H_{21}$, 3.82—OCH_3, 4.31—OCH_2 of O–$C_{10}H_{21}$, 5.344—=CH–Ar, 6.380—=CH–CO–, 6.90 and 8.04—P-Sub. Phenyl ring with the difference groups, 7.26—P-Sub. Phenyl ring with the two same like groups.

NMR confirms the structure.

IR: in cm^{-1}

Octyl.

2854.5 cm^{-1} confirms alkyl group, 1685.7 cm^{-1} and 1168.8 cm^{-1} confirms COO= group and ether group, 844.8 cm^{-1} confirms p-sub. Phenyl ring, 721.3 cm^{-1} confirms polymethylene of C_8H_{17}, 698.2 cm^{-1} confirms cis–CH=CH– group.

IR confirms the structure.

Dodecyl.

2960.0 cm^{-1} confirms alkyl group, 1257.5 cm^{-1} and 1685.7 cm^{-1} confirms –COO– group, 1168.8 cm^{-1} confirms ether group, 941.2 cm^{-1} confirms trans–CH=CH– group, 844.8 cm^{-1} confirms p-sub. Phenyl ring, 721.3 cm^{-1} confirms polymethylene of $C_{11}H_{22}$.

IR confirms above structure.

For Series-Y

NMR:

Propyl.

1.84—CH_2–CH_2–CH_3, 3.806—O–CH_3, 4.00—O–CH_2 of O–CH_2–CH_2–CH_3, 4.44 and 4.02—CH=CH–, 6.43 and 6.94, 6.97 and 7.20—P-sub. phenyl two p-sub. benzene, 7.23 and 7.55, 8.09 and 8.12—P-sub. phenyl two p-sub. benzene.

NMR confirms the structure.

Octyl.

1.81—O–CH_2–CH_2–$(CH_2)_5$–CH_3, 3.8—O–CH_3, 4.034—O–CH_2 of (O–CH_2–$(CH_2)_6$–CH_3), 4.41—CH=CH–, 6.38 and 6.43, 7.23 and 7.24—two p-sub. phenyl ring, 7.55 and 7.58, 8.09 and 8.12—two p-sub. phenyl ring.

NMR confirms the structure.

IR: in cm^{-1}

Pentyl.

720.0 cm^{-1} Poly –CH_2 (long methyl chain), 1050.0 cm^{-1} confirms ether group of ester(-COO), 820.0 cm^{-1} confirms p-sub. benzene ring, 1250.0 cm^{-1} confirms >C=O bend, 698.2 cm^{-1} confirms cis–CH=CH– group, 1750.0 cm^{-1} confirms > C=O of ester, 3000.0 cm^{-1} confirms >C-H of aromatic group.

IR confirms the structure.

Tetradecyl.

1050.0 cm^{-1} confirms >C-O of ester group, 650.0 cm^{-1} confirms cis–CH=CH–group

1250.0 cm^{-1} confirms >C=O of ester group, 840.0 cm^{-1} confirms p-sub. benzene ring

750.0 cm^{-1} confirms poly –CH$_2$- of n-octyl, 1750.0 cm^{-1} confirms > C=O of ester group

1250 cm^{-1} confirms >C=O of ester group, 3000.0 cm^{-1} confirms =C-H of aromatic group.

IR confirms the structure.

Results and Discussion

n-Alkoxy benzoic acids and n-alkoxy cinnamic acids are dimeric through hydrogen bonding. Dimerization disappears as a result of breaking of hydrogen bonding on esterification to give p-hydroxy methyl cinnamate. Thus, transition temperatures of homologs of series (X) and (Y) are relatively lower than the corresponding n-alkoxy acids from which final products are obtained. p-Hydroxy methyl cinnamate is nonmesomorphic but on linking with n-alkoxy phenyl ring through central bridge mesomorphic characteristics are exhibited, except for the first and/or second homologs for the series under comparison. Homologs of the series (X) and (Y) are entirely nematogenic without exhibition of any smectic character even in the monotropic condition except first and/or first and second homologs, respectively.

Transition temperatures of homologous series from Table 1 are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal, smooth curves are drawn through the like or related points, the phase diagrams obtained are shown separately in Figs. 1 and 2, respectively. From the phase diagrams of Figs. 1 and 2, the solid-isotropic or solid-nematic transition curves partly follow zigzag path of rising and falling and behave in normal manner. Nematic isotropic transition curves also behave in normal manner.

Nonmesomorphic behavior of first one or two homologs is attributed to their high crystallizing tendency arising out from their strong intermolecular attractions due to the presence of left shorter methyl and ethyl end groups linked through with phenyl ring. Enantiotropic nematogenic mesophase exhibited by the ethyl or propyl to hexadecyl derivatives of series (X) and (Y), respectively, is due to the maintenance of statistically parallel orientational order of

Table 1. Homologous series (X) and (Y): Transition temperatures

		Transition temperatures in °C					
		Smectic		Nematic		Isotropic	
		series		series		series	
Sr. no.	n-alkyl group	(x)	(y)	(x)	(y)	(x)	(y)
1.	Methyl	–	–	–	–	143.0	178.0
2.	Ethyl	–	–	96.0	–	107.0	170.0
3.	Propyl	–	–	88.0	124.0	108.0	140.0
4.	Butyl	–	–	78.0	115.0	118.0	128.0
5.	Pentyl	–	–	62.0	118.0	98.0	125.0
6.	Hexyl	–	–	58.0	112.0	110.0	128.0
7.	Heptyl	–	–	62.0	–	102.0	–
8.	Octyl	–	–	66.0	125.0	105.0	150.0
10.	Decyl	–	–	65.0	120.0	103.0	166.0
12.	Dodecyl	–	–	83.0	135.0	109.0	175.0
14.	Tetradecyl	–	–	79.0	132.0	99.0	163.0
16.	Hexadecyl	–	–	79.0	130.0	96.0	138.0

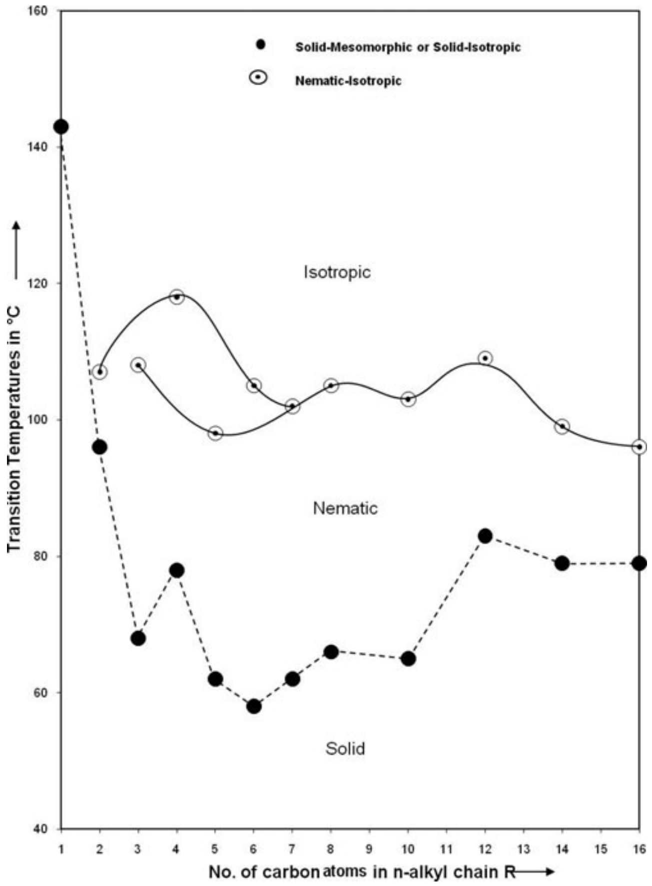
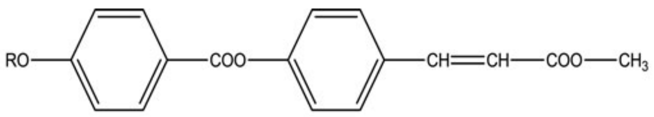


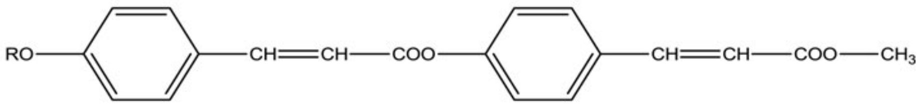
Figure 1. Methyl p-(p′-n-alkoxy benzoyloxy) cinnamates (series X).

two-dimensional array of molecules in floating condition. Thus, methyl and/or ethyl derivatives are unable to resist the thermal vibrations and passed directly into isotropic liquid without passing through any mesomorphic state whereas the rest of the homologs, i.e., ethyl (series X) or propyl to hexadecyl derivatives are capable to resist the thermal vibrations and consequently exhibit nematic mesophase without exhibition of any smectic mesophase.

The structurally similar homologous series (x) and (y) are as under:



Series X (R= C_nH_{2n+1}, n= 1,2,3,4,5,6,7,8,10,12,14,16)



Series Y (R= C_nH_{2n+1}, n= 1,2,3,4,5,6,7,8,10,12,14,16)

Scheme 2. Series X and series Y.

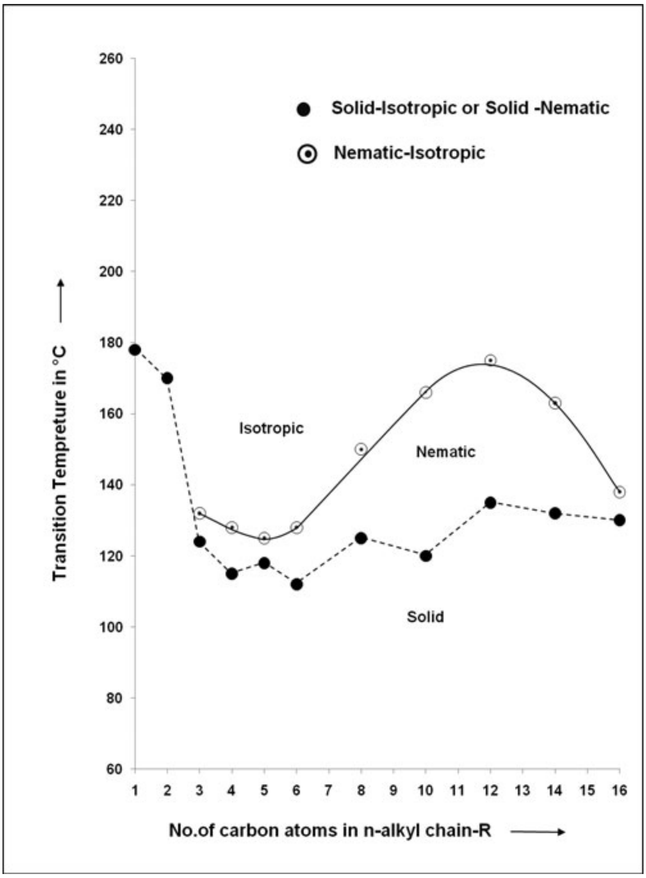


Figure 2. Homologous series: methyl p-(p′-n-alkoxy cinnamoyloxy) cinnamates (series Y).

In Figs. 4 and 5, we represents the three-dimensional (3D) diagram of series X and series Y having different central linkage group and exhibit different mesomorphic properties. The mesomorphic properties of substances depend upon polarity, polarizability, aromaticity, linearity, length to breadth ratio, geometrical shape and size, pai electron density, and many other factors of molecules, which contribute to the net intermolecular forces of attractions and hence to the mesomorphic properties and the degree of mesomorphism.

Figure 3. 3D diagram of series X (R = side chain).

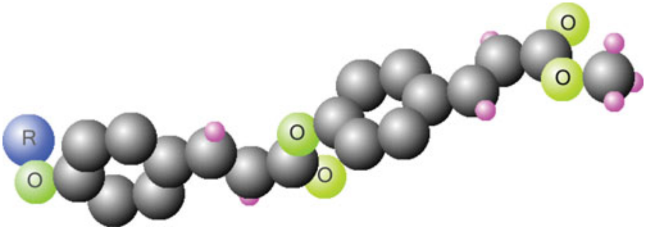


Figure 4. 3D diagram of series Y (R = side chain).

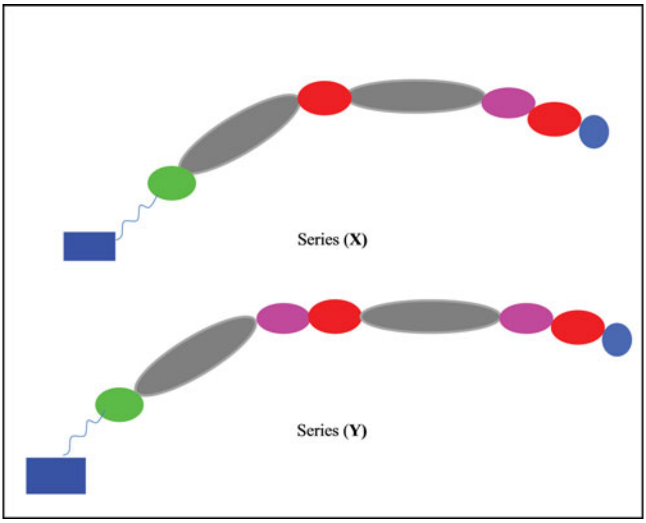


Figure 5. Space filling diagram of series (X) and series (Y).

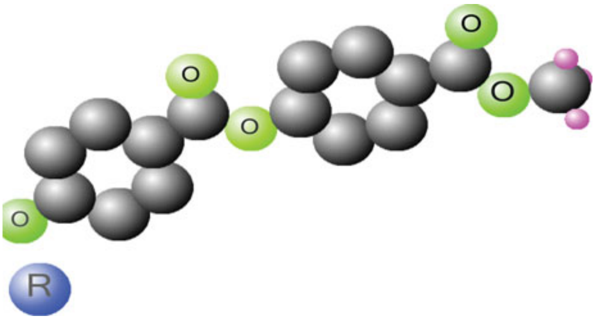


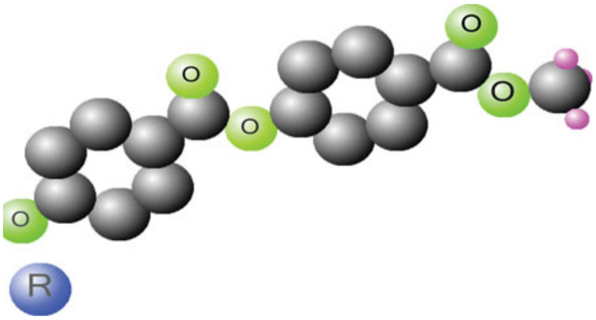
Figure 6. 3D arrangement of the atoms in series (Z) (R = C_nH_{2n+1}).

Suspicious observation of the general structure of molecules is shown in Figs. 3 and 4. In Fig. 6 of series (X) and (Y), it is clear that, geometrical shape of molecules is linear rod like without any lateral substitution. Both molecules consist of left n-alkoxy terminal, two phenyl rings, and –CH=CH–$COOCH_3$ right terminal. They differ only with respect to central bridges for the same homologs from series to series. Molecules of (X) homologous series link two phenyl rings through –COO– (ester) central bridge while, that of series (Y) link two phenyl rings through –CH=CH–COO- central bridge (Scheme 2). Thus, aromaticity due to two phenyl rings of molecules, left n-alkoxy terminals, right –CH=CH–$COOCH_3$ terminal, and linearity remains unchanged while length of molecules due to –CH=CH– part of central bridge and its unsaturation for series (Y), i.e., central bridges, viz., –COO– and –CH=CH–COO- differs. Therefore, length to breadth ratio, arrangement of atoms in space, net polarity, and polarizability cause differences of inter molecular forces of attractions and hence the difference in mesogenic characteristics of series (X) to series (Y).

In comparison transition temperatures of series (X) are relatively lower than transition temperatures of series (Y) for the same homolog from series to series. This difference of transition temperatures can be directly linked to the difference in intermolecular forces of attractions caused by the difference in length by –CH=CH– and length to breadth ratio resulting into difference in polarity as well as polarizability of molecules. In spite of lowering of transition temperatures of homologs of series (X), it is observed that the overall phase length or degree of mesomorphism (only Nematic) exhibited by series (X) is more than (maximum 52.0 °C for series (X) and 46.0 °C for series (Y)) the corresponding homologues of series (Y). Thus, two-dimensional array of the molecules even in the floating condition maintains more statistically parallel orientational order, resisting thermal vibrations in case of series (X) than series (Y). Average thermal stability for nematic–mesophase for homologous series (Y) is more than homologous series (X).

Generally, ester homologous series are smectogenic, however present two homologous series are nematogenic, i.e., smectic mesophase is totally absent. The exhibition of smectic mesophase, the degree of smectogenic character, and early or late commencement of smectic mesophase depend [11–15] upon the extent of noncoplanarity caused by the molecules. The terminal end group in the molecules of both the series under discussion bear –CH=CH–COO- functional group with a double bond. The presence of double bond can cause cis–trans isomerism and arrangement of atoms in space may operate and create such an extent of noncoplanarity of molecules that smectic mesophase formation, i.e., arrangement of sliding layer formation of molecules during course of heating the sample, is not maintained or say, fully eliminated till the last homolog and only statistically parallel orientational order of molecules is maintained in floating condition. Thus, nematic mesophase is occurred at the cost of smectc mesophase [16–21].

In comparison the type of mesomorphic phase exhibited by (X) and (Y) homologous series with a series (Z) and Fig. 6, i.e., methyl-p-(p′-n-alkoxy benzoyloxy) benzoates with its structure is as follows:



Series Z is entirely smectogenic without exhibition of any nematogenic characteristic. Thus a series (Z) is smectogenic while series (Y) and (X) are nematogenic. Hence, same central bridge and terminal groups bearing –COO– (series Z) is smectogenic and a same central and terminal group bearing –CH=CH–COO- (series Y) is nematogenic. Thus, –COO– group can induce smectic character more favorably and –CH=CH–COO– group can induce nematogenic character more favorably. Replacement of –COOCH$_3$ terminal group by –CH=CH–COO–CH_3 terminal (series Y) wonderfully causes emergence of nematic mesophase from smectic mesophase (series Z). Hence –CH=CH–COO– is strong enough to emerge nematic character from smectic character and vice versa. Thus, group efficiency order derived from induction of smectic and or nematic characters are as under.

Smectic character group efficiency order: –COO– > –CH=CH–COO–

Nematic character group efficiency order: –COO–> –CH=CH–COO–

Conclusion

In summary, ester homologous series are not necessarily the smectogenic but it may be entirely smectogenic or entirely nematogenic or partly smectogenic and partly nematogenic. We were able to compare mesomorphism property of series (X) and series (Y) with series (Z), which contain on both the side only ester linkage group and exhibit smectogenic behavior without any kind of nematogenic property.

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