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The Effect of Laterally Substituted Methoxy Group on Mesomorphicity

Jwalant j. Travadi¹

¹ Kamani Sc. and Prataprai Arts College, Amreli, Gujarat, (India).

Abstract: To understand structure-activity relationship, comparative A study of newly synthesised homologous series with structurally similar known homologous series is carried out. Newly synthesised homologous series 1 to 7^[6-12] and selected other series-X and -Y^[13-23] for comparative study, resemble to each other in all respect i.e. two phenyl rings, central bridge -COO-, right handed tail -CH=CH-COOR, left n-alkoxy end-group for the same homologue, but differs with respect to laterally substituted -OCH₃ group. Especially this study is focused to understand the effect of laterally substituted methoxy group on mesomorphicity. Different liquid crystalline properties (viz. type of mesophase, mesophase length, and relative thermal stabilities, upper transition temperatures etc are mutually compared. 1) Presence and/or absence, 2) Size 3) Position and 4) Polarity of laterally substitution of methoxy group affect the mesomorphic characteristics of similar type compounds. A phenomenon of mesomorphism is very sensitive and susceptible to molecular structure of a substance. Present comparative study supports the views and conclusions drawn earlier.

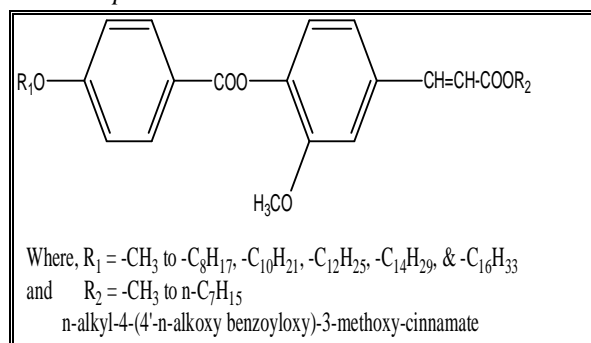
Keywords: Smectogenic, nematogenic, mesophase length, structure-activity relationship, polarity, steric effect

I. INTRODUCTION

Some substances possess ability to flow as liquid and optical properties as crystal since they are recognize as mesomorphic state^[1] known as a special state of matter. Liquid crystalline (LC) state of a substance is well known for its importance in various fields of applications^[2, 3, 4, 5]. Liquid crystalline properties are strictly depends on molecular geometry of mesomorphs and they vary by varying molecular aromaticity, central groups, terminal groups, positions of same or different functional groups on phenyl ring or rings, geometrical shape, size, polarity and polarizability etc. This is because of factors (like length to breadth ratio, net polarity and polarizability of molecules, intermolecular hydrogen bonding, effect of size and polarity of lateral substituent as well as terminal end groups etc) affecting predominantly to liquid crystallinity of material (e.g. type of mesophase, thermal stability, mesophase length, early and late commencement of mesophase in series). Present study is focused to understand structure-activity relationship with respect to study of the effect of laterally substituted methoxy group on mesomorphicity. Here comparative study among different homologous series with similar type of geometry and structural features has been carrying out.

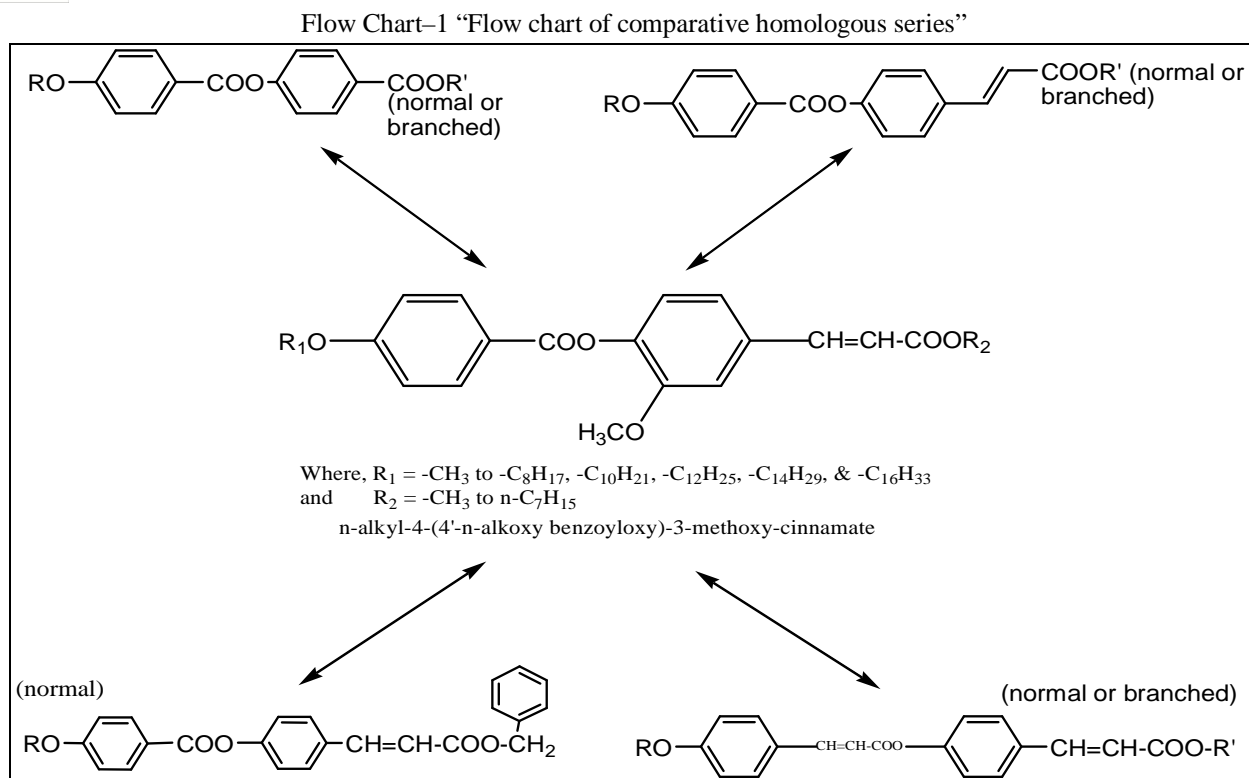
II. MATERIALS AND METHODS

A. General Formula Of Newly Synthesised Compounds



B. Comparative study

Comparative study of newly synthesised homologous series with structurally similar known homologous series is carried out. Newly synthesised homologous series 1 to 7^[6-12] and selected other series-X and -Y^[13-23] for comparative study, resemble to each other in all respect i.e. two phenyl rings, central bridge -COO-, right handed tail -CH=CH-COOR, left n-alkoxy end-group for the same homologue, but differs with respect to laterally substituted -OCH₃ group, which are reflected in "Flow Chart-1.



III. RESULTS AND DISCUSSION

A novel homologous series ($R_2 = C_1$ to C_4) of esters with two phenyl rings and lateral substitution are partly smectogenic and partly nematogenic, while novel homologous series ($R_2 = C_5$ to C_7) are totally smectogenic without exhibition of nematic property.

All novel homologous series are middle ordered melting type with considerable mesophase length temperature range.

Comparison of presently investigated series with other structurally similar known series is carry out with respect to structural geometry and liquid crystalline properties (viz. type of mesophase, mesophase length, relative thermal stabilities, upper transition temperatures etc) to understand structure-activity relationship (especially to understand the effect of laterally substituted methoxy group on mesomorphism).

High smectic phase stability is largely attributed to; (i) efficient filling of space by bulky $-OCH_3$ group, which enhances intermolecular attractions. (ii) favourable lamellar packing afforded by the polarity of the lateral $-OCH_3$ group. (iii) large size of laterally substituted $-OCH_3$ group hinders parallel arrangement of molecules which reduce end-to-end intermolecular attractions favourable to exhibit nematic properties. (iv) lateral group at ortho position with respect to $-COO-$ central bridge, {a} increase molecular breadth, reduces the strength of the lateral intermolecular attraction. {b} increases in molecular breadth which decreases the thermal stability of the nematic mesophase. (v) Polarity of $-OCH_3$ group affect π -electron conjugation, electron density on phenyl rings etc which might major effect on mesomorphic characteristics of compound.

The polarity of laterally substituted functional group in combination with the ratio of polarity to polarisability of lateral substituent affect directly net intermolecular attractions and therefore, the nature of lateral functional group, might alter, induce or diminish liquid crystalline properties.

Steric effect of the bulky substituent prevents a close molecular packing, and thus the liquid crystalline order may more easily destroyed by thermal fluctuations.

IV. CONCLUSION

- A. Present investigation may be useful for the study of binary systems to operate LC devices at desired temperature between 60°C to 100°C and agricultural production.
- B. Ester derivatives containing $-CH=CH-$ unit may be useful in agricultural production.
- C. Some of the transition temperatures varies between 36°C to 96°C for mesomorphic homologues. Such mesomorphs are useful for the study of binary systems for the devices workable at room temperatures.

- D. Suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of molecular rigidity and/or flexibility can induce mesomorphic behaviours in a substance.
- E. Favourable molecular rigidity and flexibility are governing mesomorphism depending on molecular structure.
- F. Phenomena of mesomorphism is very sensitive and susceptible to molecular structure of a substance.
- G. Present comparative study supports the views and conclusions drawn earlier.
- H. Present comparative study might be useful to the groups of researchers to design new liquid crystals with desired liquid crystalline properties (viz. mesophase, mesophase length, and relative thermal stabilities, upper transition temperatures etc).

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