SUMMARY

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5.A. New Homologous Series:

The present work incorporates synthesis of nine new homologous series, each consisting of twelve compounds, thus making the number of new compounds 108. Out of these one hundred and eight new compounds twentynine are non-mesomorphs, particularly the last two homologous series C-8 and C-9. The rest of new compounds are mesomorphic in character, though the range of temperature over which they exhibit mesomorphism varies from just 1°C to about 60°C. Thirty-nine compounds are pure nematogens and eighteen are pure smectogens while twenty-two exhibit polymesomorphism.

The first seven mesomorphic homologous series are high melting mesogenic series; of these the first four A-1 to A-4, are with straight chain linking whereas the next three series, B-5 to B-7, are with 'iso' linking. The last two non-mesogenic homologous series viz. C-8 and C-9 have chloro substituent in the meta and ortho position respectively.

The molecules of these nine homologous series have many features in common such as

(i) two benzene rings,

(ii) one central linkage,

(iii) common alkoxy terminal substituents with varying alkyl chain length from the first to the last homologues, at the left end,

(iv) and therefore almost the same length and breadth.

They differ, however, in the following respects:

i) the terminal substituents at the right end are different in first seven series viz. A-1 to A-4 and B-5 to B-7.

(ii) the C-8 and C-9 homologous series have lateral substituents either at ortho or meta positions.

With above similarities and differences, a beautiful display of molecular forces arising from dipolar nature; polarizability and other factors are seen affecting the mesomorphic properties. Other factors as well, which affect them one way or the other, like length and breadth of the molecules, length to breadth ratio and the ratio of terminal to lateral attractions, nonplanarity of the molecules and steric hindrance, are seen working in combination maintaining a balance or establishing a predominance of one set of them over the other.

The high melting character of the mesomorphic homologous series is discerned by the falling tendency of the nematic--isotropic transition curves.

Exhibition of polymesomorphism is quite characteristic of the molecular geometry of the homologues. The smectic-nematic

transition curves rise steeply but smoothly and assume a dome shape which establishes the increasing character of the smectic property as the alkyl chain length of the terminal groups increases.

The various transition temperatures are not quite high and mesophase lengths are also generally about 20° to 30°C. The nematic property does not prevail upto the last member, exception being series A-1, and about the last three homologues are pure smectogens. It is also of interest to note that the overall mesomorphic property too decreases as the alkyl chain length increases. However, it is in this context that the increasing character of the smectic property as the alkyl chain length increases assumes a very striking significance.

As the alkyl chain length increases at the right terminals of the two clusters of homologous series, A-1 to A-4 and B-5 to B-7, the overall polarizability of the molecules increases which is conducive to decreasing nematic character and increasing smectogenic property, in combination comes the increasing chain length at the left terminal influencing almost the same way. The balanced play of these molecular forces and the modulation in the mesomorphic variations are very well established by these seven homologous series.

The nematic thermal stability for the homologous series, alternating though, is of decreasing order as the alkyl chain

length increases. The odd-even effect for the N-I transition curves is clearly marked; however, with increasing alkyl chain length, the alternating effect becomes more marked as one moves from A-1 series to A-4 series or B-5 to B-7 series. It may, thus, be said that the overall polarizability of the molecules is more responsible for the odd-even effect than any other factor.

The solid-mesomorphic transition curves show, by and large, the classical behaviour as mostly observed in such homologous series; however, in certain series, their path seems to be more responsible for the mesomorphic range of the homologues, rather than other factors. It would, therefore, appear quite logical to study the behaviour of these transitions in greater details. This study has brought forth sufficient evidence of solid-solid transformations.

This study has also provided the evidence for the impact of the 'iso' linking of the terminal alkyl chain of a homologue exhibiting mesomorphism. With 'iso' linking, the molecules acquire a proportionately greater breadth while simultaneously the length is decreased to the extent of a carbon atom link. The transitions are proportionately lowered. It may, thus, be concluded that the increased breadth due to'iso' linking causes the transitions to depress; while this effect is on both smectic and nematic transitions, it is pronounced on nematic properties.

It is of interest to note further that the decreased transitions due to 'iso' linking when A-2 series is compared with B-5 series, is rather slightly made up when A-1 series is compared with B-5 in whose cases the length of the molecule is comparable. Likewise clusters (i) A-3, B-6 and A-2, B-6 and (ii) A-4, B-7 and A-3, B-7 may be compared. The combination of these three clusters of the series brings forth the effects of (i) breadth alone due to 'iso' linking and (ii) breadth coupled with proportionate decrease in length. However, more such series will have to be studied if a fair quantitative estimate for (i) and (ii) above is to evolve.

The last two homologous series viz. C-8 and C-9, with chloro substituent in meta and para position respectively, are non-mesomorphic. Though the melting points are lowered considerably as compared to C-10 series where chloro substituent is at para position, it fails to exhibit mesomorphism. The chloro substituent in the lateral positions push the molecules away and make the solid structure such that yields to thermal agitation easily and passes into isotropic liquid without exhibiting mesomorphism. The lateral substituent increases the breadth of the molecule and as the series comprise of only two phenyl rings, it seems that length to breadth ratio is not conducive to the mesomorphism.

The orders of nematic and smectic thermal stabilities, as emerging from the study of the present seven series, for the

various groups are :

Nematogenic order

A-1 to A-4 series

$-OC_2H_5 > -OC_4H_9 > -OCH_3 > -OC_3H_7 > -OC_5H_{11}$

B-5 to B-7 series

$iso\text{-}OC_3H_7 < iso\text{-}OC_4H_9 < iso\text{-}OC_5H_{11}$

Smectogenic order

A-1 to A-4 series

$-OC_4H_9 > -OC_5H_{11} > -OC_2H_5 > -OC_3H_7 > -OCH_3$

B-5 to B-7 series

$iso\text{-}OC_5H_{11} > iso\text{-}OC_4H_9 > iso\text{-}OC_3H_7$

Pure nematogens in all the series exhibit threaded texture while the polymesomorphs exhibit homeotropic threaded texture. The smectic property exhibits fan shape focal conic smectic A in almost all polymesomorphs while some smectogens exhibit homeotropy. Mesomorphic textures are determined by the optical method.

The DSC application to homologues of A-1 to A-3 series has confirmed the probability of hypothesis of a solid-solid transformation prior to the induction of mesomorphic character as the leading clue to the solid-mesomorphic transitions' erratic pattern. More studies of this type will be, however, required to be carried

out before a plausible conclusion can be drawn. This also indicates that the x-ray study for the solid state of these homologues will turn out to be quite fruitful.

The transitions obtained by the DSC system have been plotted versus the number of carbon atoms, the phase diagrams for the A-1 to A-3 series resemble very much those obtained by the optical method. Additional information regarding the solid-solid transitions are given in the plot from DSC data, the monotropic transitions were not confirmed as the cooling system was not in working condition.

The plots of total ΔS versus the number of carbon atoms in the alkyl chain, show the alternation effect for the nematic-isotropic transitions as well as the falling tendency of the nematic property as the number of carbon atoms increases in the alkyl group at the left terminal.

5.B. Mixed Mesomorphism:

Sixteen binary systems have been investigated in this study and the results are highly interesting and captivating. Both components of these systems are homologues of the same homologous series (System No.1 to 11), while in system No.12 to 16 the components are from two different homologous series viz. C-8 and C-9. As such, the components are identical in their molecular structure in almost all respects. The difference is

in the higher or lower homologues of the same series (system No.1 to 11) or the same homólogue from two different series viz. C-8 and C-9 (System No.12 to 16).

Mostly the components of the systems studied differ by one or two methylene, $-CH_2-$, units or in the position of the chloro substituent. In the system No.5 both the components are non-mesomorphic but most of the compositions of the two, exhibit nematic mesophase while in systems like system No.6 and 9, monotropy of the mesophase of one component is transformed into enantiotropy by non-mesomorph and enantiotropic nematogen respectively. In the system No.7 and 8 monotropy remains unaltered through out the system. Not a single system could induce smectic characteristic from non-smectogenic components.

It became possible to evaluate the impact of increase in the alkyl chain length by one or two methylene units on mixed mesomorphism as the components mostly differ by one or two methylene units. Mixed polymesomorphism of much wider range is obtained though in terms of extended mixed mesophase length, it is the smectic property which is at advantage over the nematic one.

Depending upon the molecular forces due to (i) polarity and (ii) polarizability as well as induced effect of the carbon atoms in the alkyl chain and (iii) the extent of sinking of the

eutectic temperature, the shapes of the transition curves in the phase diagrams assume concavity or convexity. This study is very well substantiated by the factors responsible for enhancing or depressing mixed mesomorphism.

The impact of molecular forces is well established in lowering the mixed mesomorphic transitions. Obtaining two or more eutectics in the phase diagrams of the binary system No.3,5, 6,7,8,9 and 11 point to formation of molecular complexes. The mixed study has provided with the clues to 'enhancing' or 'depressing' factors for the mesomorphic character.

System No.12 to 16 have non-mesomorphic components from the non-mesomorphic homologous series C-8 and C-9 and they fail to exhibit liquid crystallinity. The molecular forces conducive to mesomorphism are not produced in any of the compositions in the mixed systems.

The entire study (i) of homologous series (ii) DSC system and (iii) mixed mesomorphism has been extremely fruitful, very interesting and revealing conclusions have been possible to draw. Good light has been thrown by this study on the existing knowledge of liquid crystals and on the probable advancement of the various aspects, it has also thrown light on the 'design' of the molecules while synthesizing a host of new compounds whose mesomorphism can display a colourful panorama as the present homologous series do.