SUMMARY

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"STUDY OF POTENTIAL MESOGENIC MATERIALS"

Following mesogenic homologous series and the systems are synthesized and their mesogenic properties are studied.

1. Mesogenic Biphenyl Derivatives

i. 4(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyls.

ii. 4-(n-Alkanoyloxy)-4'-nitrobiphenyls.

iii. 4-n-Alkoxy-4'-nitrobiphenyls.

2. Cholesteryl Derivatives

iv. Dicholesteryl carbonates with flexible and rigid spacers.

v. Dicholesteryl carbamates.
vi cholesteryl 4-n-alkoxy phenyl carbamates
vii. Dicholesteryl imide esters.

3. Chiral Ester Amides.

viii S(+)-4(4'-β-methyl butoxy benzoyloxy)-4"-n-alkoxy benzoyloxy benzanilides.

4. New mesogens with typical structural units.

(a) N-phthaloyl derivatives.

(b) Mesogenic dimers with biphenyl nuclei.

(c) Azoacids and a chiral schiff base esters.

5. Fluorescent mesogenic polymers with chalcone linkage.

P_1 Polyester with two 'oxyethylene' spacers and a chalcone linkage.

P_2 Polyester with three 'oxyethylene' spacers and a chalcone linkage.

P_3 Polyester with four 'oxyethylene' spacers and a chalcone linkage.

6. Textures of different phases and characterization of smectic phases by miscibility study.

7. Calorimetric study.

1. Mesogenic Biphenyl Derivatives.

Three homologous series are synthesized and their liquid crystalline properties are studied.

I. 4-(4"-n-Alkoxybenzoyloxy)-4'-nitrobiphenyls.

Thirteen compounds have been synthesized and their mesogenic properties were evaluated. The methoxy to n-propoxy derivatives exhibit nematic mesophases. Smectic mesophase appears from n-butoxy derivative as monotropic phase. n-Butoxy to n-octyloxy derivatives exhibit smectic and nematic phases. n-Decyloxy to n-octadecyloxy derivatives exhibit only smectic phases.

II. 4(n-Alkanoyloxy)-4'-nitrobiphenyl.

Seven members of the series are synthesized. In this series only higher homologues are synthesized as mesophase commences from heptyl derivative(octanoate) as monotropic nematic phase. Nematic phase remains monotropic throughout the series i.e. upto nonyl derivative. Smectic phase commences from nonyl derivative as monotropic phase. n-Undecyl derivative to n-pentadecyl derivatives exhibit enantiotropic smectic phases.

III. 4-n-Alkoxy-4'-nitrobiphenyl.

Eventhough some members were reported by Gray, the whole series was synthesized to compare the mesogenic properties with series I and II. n-Heptyloxy to n-hexadecyloxy derivatives exhibit mesomorphism. Gray has reported monotropic nematic mesophase for n-pentyloxy and n-hexyloxy derivatives. In the present study monotropic nematic phases could not be observed. Gray has reported enantiotropic nematic phase for n-octyloxy derivative where as in the present study this phase could not be observed. Except those three cases the mesogenic properties are comparable with the reported one.

All the three homologous series exhibit mesomorphism. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain does not exhibit prominent odd-even effect for nematic-isotropic transition temperatures. Odd-even effect is observed only up to second member of the series I. Smectic-nematic transition temperatures do not exhibit odd-even effect and rises steeply.

The plot of transition temperatures versus number of carbon atoms in the alkoxy chain exhibits smooth rising curve in the case of series II and III. Mesophases commence very late in the series hence odd-even effect can not be observed for nematic-isotropic, smectic-nematic or smectic-isotropic transition temperature curve.

A few binary systems where one of the component is from each series I, II and III are studied. One of the binary systems exhibit mesophases below room temperature and mesophase persists above room temperature.

2. Cholesteryl Derivatives

IV. Dicholesteryl carbonates with flexible and rigid spacers.

Thirteen dicholesteryl carbonates with flexible and rigid spacers are synthesized and their mesogenic properties are studied. Except for two,all the compounds exhibit mesomorphism. All the mesogenic compounds exhibit cholesteric phase with one exception. All these compounds have very high super-cooling tendency. Cholesteric phase persists upto room temperature in some mesogens.

V. Dicholesteryl Carbamates

Seven dicholesteryl carbamates are synthesized with flexible and rigid spacers. Out of seven, six compounds are exhibiting smectic phases, whereas one compound is exhibiting only cholesteric phase. Transition temperatures are plotted against number of methylene spacers. Marked odd-even effect is not observed in the smectic-Isotropic transition temperature curve. The solid-smectic transitions also do not exhibit marked odd-even effect. Compound with 1,4-phenylene substitution exhibits cholesteric phase.

VI Cholesteryl 4-n-alkoxyphenyl carbamates.

Thirteen members of this series are synthesized. Methoxy and n-propoxy derivatives exhibit monotropic smectic and enantiotropic cholesteric phases. Ethoxy derivative exhibits only cholesteric phase. n-Butoxy derivative exhibits enantiotropic smectic and cholesteric phases. n-Pentyloxy to n-octadecyloxy derivatives exhibit only smectic phases. The mesogenic behaviour indicates that series exhibits smectogenic tendencies. The plot of number of carbon atoms against the transition temperatures exhibits odd-even effect for cholesteric-isotropic transitions upto fourth member only. The smectic-cholesteric transition temperature curve rises steeply and merges with cholesteric-isotropic transition temperature curve from n-pentyloxy derivative giving smectic-isotropic transition temperature curve, which exhibits falling tendency as series is ascended.

VII. Dicholesteryl imide esters.

Six compounds are synthesized by varying methylene spacers. Except one, all the compounds are exhibiting cholesteric phases. The solid-mesogenic transition temperatures are above 200 °C. The plot of transition temperatures against the number of methylene spacers exhibits odd-even effect for cholesteric-isotropic transition temperatures as well as for solid-cholesteric transition temperatures.

In the present study it was observed that dicholesteryl carbonate exhibit cholesteric phases, whereas dicholesteryl carbamates exhibit smectic mesophases. This indicates that carbamate linkage is more conducive to smectic mesomorphism. Dicholesteryl imide esters exhibit only cholesteric phases.

3. Chiral Ester Amides

VIII. S(+)-4(4'-β-methyl butoxy benzoyloxy)-4"-n-alkoxybenzoyloxy benzanilides.

Eleven members of this series are synthesized. Cholesteric mesophase commences from the n-butoxy derivative as monotropic phase. n-Pentyloxy to n-decyloxy derivatives exhibit enantiotropic cholesteric phases. n-Dodecyloxy derivative exhibits smectic phases (SmA and SmB) and cholesteric phase. n-Tetradecyloxy to n-octadecyloxy derivatives exhibit $S_m{}^{*}C$ and $S_m{}^{A}$ phases. The plot of transition temperatures versus carbon atoms does not exhibit any odd-even effect for cholesteric-isotropic transition temperatures. Smectic A-isotropic transition temperature curve exhibits a smooth trend. Sm*C - SmA transition temperature curve falls initially then shows rising tendency as expected in the higher homologues.

4. New mesogens with typical structural units.

The study indicated that cholesteryl N-phthaloyl derivatives with even aliphatic short spacer exhibit mesomorphism. The aromatic 1,4-substituted phenyl ring enhances mesomorphism.

Dimers of 4-hydroxy-4'-nitro-biphenyl with 1,4-phenylene and trans 1,4-cyclohexylene central core exhibits nematic mesophases of comparable thermal stabilities.

The aromatic azo acid with flexible terminal methylene spacers exhibits mesomorphism. Chiral ester schiff base exhibits polymorphism of smectic phases where chiral smectic *C phase is observed as monotropic phase. Number of new such compounds are now being prepared as the extension of this work.

5. Fluorescent mesogenic polymers with chalcone linkage.

In the present study three polyesteric chalcones with different 'oxyethylene spacers' are synthesized. Out of three, two polymers exhibit nematic mesophases and one does not exhibit birefringence, but the polymer melt on slight disturbance exhibits intense birefringence and on cooling solidifies as a glassy material. The solution viscosity studies were carried out for all the three polymers. The intrinsic viscosity varies from 0.125 to 0.165. All the polymers are fluorescent in nature as shown by fluorescent spectra.

6. Textures of different phases and characterization of smectic phases by miscibility study.

(a) The nematic phases exhibit classical thread like texture and marble texture.

(b) The cholesteric phases exhibit plane textures and focal-conic textures.

(c) Most of the smectogens exhibit focal-conic or fan shaped texture. They are mainly smectic-A type. A few chiral smectogens exhibit schilieren texture of chiral smectic *C phase.

The smectic phases are further characterized by contact method. The study indicates that most of the compounds exhibit smectic A phase.

The microphotograph representing texture are given in the thesis.

7. Calorimetric study.

The phase behaviour of six series are studied by differential scanning calorimeter. Some members of series exhibit prominent solid-solid transitions. This could be achieved by combining DSC and microscope study. The enthalpy and entropy changes exhibit normal odd-even effect

All the compounds are characterized by elemental analysis and spectroscopic studies.