LIQUID CRYSTALS WITH NOVEL STRUCTURAL UNITS

SUMMARY

SUBMITTED TO

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

FOR

THE DEGREE OF

Doctor of Philosophy

(APPLIED CHEMISTRY)

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MARCH - 1998

SUMMARY

LIQUID CRYSTALS WITH NOVEL STRUCTURAL UNITS

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

1 Low melting smectogenic esters with broken alkoxy chain.

i) Ethoxyethyl 4(4'-n-alkoxybenzoyloxy)benzoates.

ii) Methoxyethyl 4(4'-n-alkoxybenzoyloxy)benzoates.

iii) Methoxyethyl *trans* -4(4'-n-alkoxybenzoyloxy) α- methyl cinnamates.

2. Liquid crystalline Schiff bases with naphthalene nucleus and azomesogens.

iv) 4-n-Alkoxybenzylidene -2'-aminonaphthalenes.

v) 4(4'-n-Alkoxybenzoyloxy benzylidene) 2'-aminonaphthalenes.

vi) 4(4'-n-Alkoxybenzoyloxy benzylidene) 2'-aminonaphthalene -1"-thiols.

vii) 4-n-Alkoxybenzylidene -4'-isopropylanilines.

viii) 4-n-Alkoxyphenyl azo -2'- naphthalenes.

ix) 4(4'-n-Alkoxybenzoyloxy) phenylazo 2"-naphthalenes.

3. Liquid crystalline homologous series with biphenyl nucleus.

x) 4(4'-Methoxy phenyl) 4"-n-alkoxy benzanilides.

xi) 4'-n-Methoxy -α-methyl biphenylidene -4"-n-alkoxy anilines.

4 Designing mesogenic materials for NLO properties.

xii) 4-Methyl 2', 4'-bis(4"-n-alkoxy benzoyloxy) azobenzenes.

xiii) 4-Methyl 2'- hydroxy -4'-(4"-n-alkoxy benzoyloxy) azobenzenes.

xiv) 4-Methyl 2'-hydroxy -4'-n-alkoxy azobenzenes.

xv) 4-Methyl 2', 4'-di -n-alkoxy azobenzenes.

xvi) 4-Methyl 2'-acetyloxy 4'-(4"-n-alkoxy benzoyloxy) azobenzenes.

5. Synthesis of biphenyl derivatives

6 Mixed mesomorphism

7 Texture of different phases and characterization of smectic phases by miscibility study.

8. Calorimetric study.

1. Low melting smectogenic esters with broken alkoxy chain.

Three homologous series are synthesized and their mesogenic properties are studied.

Series - I : Ethoxyethyl 4-(4'-n-alkoxybenzoyloxy) - benzoates.

Twelve compounds have been synthesized and their mesogenic properties are evaluated.

First four members are non-mesogenic. n-Hexyl and n-octyl members exhibit enantiotropic smectic A phase whereas rest of the members exhibit monotropic smectic A phases.

Series - II : Methoxyethyl 4(4'-n-alkoxybenzoyloxy) benzoates.

Twelve compounds have been synthesized and their mesogenic properties are evaluated.

First four members are non-mesogenic, n-pentyl and n-hexyl derivatives exhibit monotropic smectic A phase, whereas rest of the members exhibit enantiotropic smectic A phases.

Series - III : Methoxyethyl *trans* -4(4'-n-alkoxybenzoyloxy)-α- methyl cinnamates.

Nine compounds of the series with alkoxy group from n-butoxy to n-octyloxy, n-decyloxy, n-dodecyloxy, n-tetradecyloxy and n-hexadecyloxy have been synthesized Lower members are non-mesogenic, n-heptyl derivative exhibits monotropic smectic A phase whereas rest of the higher members are enantiotropic smectic A.

All the three series are smectogenic in nature and exhibit smectic A mesophases. The plot of transition temperatures against number of carbon atoms in the alkoxy chain, shows odd-even effect for only series - I whereas series - II and series - III do not show any odd-even effect. All the three series exhibit rising tendency for smectic - isotropic transition tempertures, which levels off for the higher homologues, except in the case of series - III.

The mesogenic behaviour of all the three series indicates that introduction of broken alkoxy group in the ester chain reduces melting points as well as transition temperatures. Due to this behaviour smectogenic mesogens are obtained which exhibit mesomorphism at room temperature.

2. Liquid crystalline Schiff bases with naphthalene nucleus and azomesogens

Series - IV : 4-n-alkoxybenzylidene -2'-aminonaphthalenes.

Twelve compounds have been synthesized and their mesogenic properties are evaluated.

The n-hexyloxy to n-Decyloxy derivatives exhibit monotropic nematic phases n-Dodecyloxy derivative exhibits monotropic Smectic A as well as monotropic nematic phase Rest of the members are non-mesogenic.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain exhibits a tendency of rising nematic-isotropic transition in ascending series

Series - V : 4(4'-n-alkoxybenzoyloxy benzylidene) -2'-aminonaphthalenes.

All the twelve members synthesized exhibit enantiotropic nematic phase Smectic C mesophase commences from the n-heptyloxy derivative as a monotropic phase. n-decyloxy to n-Hexadecyloxy derivatives exhibit enantiotropic Smectic C phase

Series - VI : 4(4'-n-alkoxybenzoyloxy benzylidene) -2'-aminonaphthalene -1"- -thiols

All the twelve members synthesized exhibit enantiotropic nematic phase Smectic C mesophase appears from the n-dodecyloxy derivative as a monotropic phase and the n-tetradecyloxy and n-hexadecyloxy homologues exhibit enantiotropic Smectic C phases.

The study has provided number of smectic C mesogens. The study also revealed that Schiff base linkage is more conducive to smectic mesophase compared to azo central linakge when all other parameters are similar Presence of terminal naphthalene nucleus enhances mesomorphism by increasing polarizability of the molecules of the series.

Series - VII : 4-n-alkoxybenzylidene -4'-isopropylanilines

Twelve compounds have been synthesized and their mesogenic properties are evaluated.

The n-octyloxy and n-dodecyloxy derivatives exhibit enantiotropic smectic A phase whereas n-decyloxy and n-tetradecyloxy derivatives exhibit monotropic smectic A phases. Rest of the members are non-mesogenic.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain exhibits a tendency of rising smectic - isotropic transition in ascending series and also indicates the steep rising tendency of solid-smectic or isotropic transition for n-decyloxy and n-tetradecyloxy derivatives which results in pronounced monotropic smectic nature.

Series - VIII : 4-n-alkoxyphenyl azo -2'-naphthalenes.

Seven compounds have been synthesized. All the compounds are non-mesogenic.

Series - IX : 4(4'-n-alkoxybenzoyloxy) phenylazo -2'-naphthalenes.

All the twelve members synthesized exhibit enantiotropic nematic phase Smectic C esophase commences from the n-decyloxy derivative as a monotropic phase.

All the three homologous series exhibit mesomorphism. The plot of transition tempertures against the number of carbon atoms in the alkoxy chain shows steady fall in nematic-isotropic transitions and exhibits marked odd-even effect. It also exhibits a tendency of rising smectic - nematic transitions in ascending series. The rising smectic-nematic transitions slightly level off for higher homologues in series V.

3. Liquid crystalline homologous series with biphenyl nucleus.

Series - X : 4(4'-methoxy phenyl) 4"-n-alkoxy benzanilides.

Twelve compounds have been synthesized and their mesogenic properties are evaluated. All the members exhibit enantiotropic mesomorphism. Methoxy derivative is purely nematogenic. Ethoxy to n-butyloxy derivatives exhibit enantiotropic smectic A as well as nematic mesophases. n-pentyloxy to -n-hexadecyloxy derivatives exhibit only enantiotropic smectic A mesophases.

Series - XI : 4'-methoxy -α- methyl biphenylidene -4"-n-alkoxy anilines.

Nine members of the series are synthesized. All the members synthesized exhibit enantiotropic nematic mesophase.

All the members of series - X and Series - XI exhibit mesomorphism The plot of transition temperatures against the number of carbon atoms in the alkoxy chain does

not exhibit odd-even effect for nematic - isotropic or smectic - nematic transition temperatures though smectic phase is observed from the second member of the series - X whereas series - XI exhibits usual odd-even effect for the nematic - isotropic transition temperatures.

The study has further enhanced the observation of Vora et al that amido central linkage enhances smectic and nematic mesophases, enhancement in smectic mesophase is more than in nematic mesophase.

4. Designing mesogenic materials for NLO properties.

Series - XII : 4-methyl 2'-4'-bis(4"-n-alkoxy benzoyloxy) azobenzenes.

Twelve compounds have been synthesized and their mesogenic properties were evaluated. n-Butyloxy to n-hexadecyloxy derivatives exhibit monotropic smectic C mesophase. The first three homologues are non-mesogenic.

Series - XIII : 4-methyl 2'-hydroxy -4'-(4"-n-alkoxy benzoyloxy) azobenzenes.

All the twelve homologues synthesized exhibit enantiotropic nematic mesophase. This series has very high thermal stability.

Series - XIV : 4-methyl 2'-hydroxy 4'-n-alkoxy azobenzenes.

This series is also purely nematogenic. n-Propyloxy derivative exhibits monotropic nematic phase. Higher members exhibit enantiotropic nematic phase

Series - XV : 4-methyl 2'-4'-di-n-alkoxy azobenzenes.

Nine compounds have been synthesized. All the compounds were found to be non-mesogenic with very low melting points.

Series - XVI : 4-methyl 2'-acetyloxy -4'-(4"-n-alkoxy benzoyloxy)azobenzenes

Twelve homologues have been synthesized. They are purely nematogenic. All the homologues of this series exhibit monotropic nematic mesophase except the n-dodecyloxy and n-tetradecyloxy homologues which are enantiotropic nematic.

All the four homologous series - XII - XIV and XVI exhibit mesomorphism The series XII exhibits monotropic low melting smectic C mesophase whereas rest of the series exhibit nematic mesophases. The plot of transition temperatures against the number of carbon atoms in the alkoxy chain exhibits marked odd-even effect for the mesophase - isotropic transitions. Series - XII exhibits a tendency of rising smectic - isotropic transition in ascending series. Series - XII, XIV and XVI shows steady fall in nematic-isotropic transition except the odd derivatives of series - XIV which shows rising tendency.

The study provided unsymmetrical smectogens exhibiting Smectic C phases which can be helpful in designing NLO material. The study also provided further understanding effect of intramolecular hydrogen bonding when phenolic hydroxy group is in the central phenyl ring. Study has opened up a major field of work in synthesis of unsymmetrical mesogens with long aromatic side arm.

The monoester and siamese twins of n-octyloxy derivative of series - XIII with adipic acid were synthesized. Interesting results were obtained.

Two metallomesogens having Cu (II) and Ni (II) as a central metal atom and n-hexadecyloxy derivative of series - XIII as a ligand have been synethesised This opens up a new field inthe synthesis of metallomesogens.

5. Synthesis of biphenyl derivatives

Seven new homologues of different homologous series containing biphenyl moiety are synthesized for the comparison of thermal stabilities of phase transitions

6. Mixed mesomorphism

Three binary systems where one of the component is from series - I or series - II are studied. One of the binary systems exhibits smectic A mesophase below room temperature and persists above room temperature.

6 1 Three binary phase diagrams were developed by doping (1R, 2S, 5R)-(-) menthyl 4-n-decyloxy benzoate with n-decyloxy, n-tetradecyloxy and n-hexadecyloxy homologues of series IX by adding dopant maximum upto 50 %

The study provides a mean to induce Smectic *C and cholesteric phase (*N) in the system by doping it with the derivative of naturally occuring chiral menthol.

7. Texture of different phases and characterization of smectic phases by miscibility study.

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

b) Smectogens exhibit focal - conic (Smectic A) or schlieren (Smectic C) texture

The nematic and smectic mesophases are further characterized by contact method.

The microphotograph representing texture are given in the thesis

8. Calorimetric study.

The phase behaviour of nine homologues of series XII and other thirteen homologues of different homologous series are studied by DSC.

Enthalpy values of different phase transitions agree well with the literature value

The plot of enthalpies and entropies for the homologous series XII exhibits regular trend.