SUMMARY

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The following ten homologous series of Schiff base compounds and three types of binary nematogenic systems have been prepared and their mesomorphic behaviour studied.

A. Naphthalene Schiff bases

1. 4-n-Alkoxy-1-naphthylidene-p-n-propoxyanilines
2. 4-n-Alkoxy-1-naphthylidene-p-n-butoxyanilines
3. 4-n-Alkoxy-1-naphthylidene-p-n-amyloxyanilines
4. 4-n-Alkoxy-1-naphthylidene-p-i-amyloxyanilines

B. p-Phenylene derivative having ester and azomethine linkages

I. Nematogenic Homologous Series

5. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-ethylanilines
6. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-phenetidines
7. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butylanilines
8. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-n-butoxyanilines

II. Smectogenic Homologous Series

9. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-cyanoanilines
10. p(p'-n-Alkoxybenzoyloxy)benzylidene-p"-nitroanilines

C. Mesogenic Mixtures

System I. Both components (A) and (B) exhibit monotropic nematic mesophase.

Component A : 4-n-Butoxy-1-naphthylidene-p-i-amyloxyaniline

K 68.5 I (50.0 N)

Component B : 4-*n*-Hexyloxy-1-naphthylidene-*p*-*i*-amyloxyaniline

K 58.0 I (51.5 N)

System II Component (A) exhibiting monotropic nematic mesophase and component (B) exhibiting enantiotropic nematic mesophase.

Component A : 4-*n*-Dodecyloxy-1-naphthylidene-*p*-*n*-propoxyaniline

K 71.0 I (57.0 N)

Component B : 4-*n*-Dodecyloxy-1-naphthylidene-*p*-*n*-butoxyaniline

$$K \xrightarrow{59.0} N \xrightarrow{67.0} I$$

System III Both components (A) and (B) exhibit enantiotropic nematic mesophase.

Component A : 4-*n*-Nonyloxy-1-naphthylidene-*p*-*n*-amyloxyaniline

$$K \xrightarrow{55.0} N \xrightarrow{64.0} I$$

Component B : 4-*n*-Dodecyloxy-1-naphthylidene-*p*-*n*-butoxyaniline

$$K \xrightarrow{59.0} N \xrightarrow{67.0} I$$

A. Naphthalene Schiff bases

All the four series (1 to 4) have comparatively low melting points. Though most of the mesogenic compounds are monotropic in nature, some members are enantiotropic mesomorphic also. The number of compounds exhibiting enantiotropic mesophase goes on increasing as the alkyl chain length increases. In the case of series 4-n-alkoxy-1-naphthylidene-p-n-butoxyanilines and p-n-pentyloxyanilines some of the compounds exhibit polymorphism i.e. they have two solid modifications. All the four series are purely nematic, the smectic mesophase is not observed even in the last members of the series. The nematic-isotropic transition temperature curve in all the series exhibit odd-even effect, the even members always occupying the upper curve. It is interesting to note that both the curves exhibit ascending tendency whereas the nematic-isotropic transition temperature curve in a normal homologous series falls smoothly with increase in the alkyl chain length.

In all these homologous series (1 to 3) an alkoxy group on one end is changed from propoxy to pentyloxy and the average nematic-isotropic transition temperatures of all these series alternate exhibiting an odd-even effect.

B. p-Phenylene derivatives having ester and azomethine linkages

I. Nematogenic Homologous Series

All the four series (5 to 8) exhibit nematogenic behaviour, i.e. first few members are purely nematic and the smectic mesophase commences from the middle members. These series differ from normal mesogenic homologous series by exhibiting smectic and nematic mesophase in the last members. All these series have large phase length and high thermal stability. The smectic mesophase commence at C_6, C_{10}, C_6 and C_7 derivatives in the series 5, 6, 7 and 8 respectively.

The nematic-isotropic transition temperatures lie on two falling curves exhibiting the odd-even effect, the even members occupying the upper curve. The smectic-nematic transition temperatures lie on smooth rising curves which do not merge with the falling nematic-isotropic curves. However, in the case of series p(p'-n-Alkoxybenzoyloxy)benzylidene-p''-n-butylanilines the smectic-nematic transition temperature curve rises to the maximum and then levels off.

The nematic phase has a threaded texture and the smectic phase has a focal conic texture. However many members of these homologous series exhibit homeotropic smectic mesophase. The transitions in the homeotropic condition are distinguished by a spec-like wave front.

All the series (5 to 8) have the same structural features except the end groups on one side, which helped to deduce group efficiency order for promoting smectic and nematic mesophase and is as under :

Nematic : $OC_2H_5 > OCH_3 > \underline{n}\text{-}OC_4H_9 > CH_3 > OH = C_2H_5 > \underline{n}\text{-}C_4H_9 > H$

Smectic : $OH > \underline{n}\text{-}OC_4H_9 > \underline{n}\text{-}C_4H_9 > C_2H_5 \approx CH_3 > OC_2H_5 > H > OCH_3$

The terminal group efficiency order deduced here broadly compare well with those of Dave and Dewar (90) Dave and Vora (91), Gray (74) and Dewar and co-workers (193).

II. Smectogenic Homologous Series

Both the series (9 and 10) would exhibit positive dielectric anisotropy as they have $-NO_2$ and $-CN$ end groups, whose dipole act along the long axes of the molecules. Both the series are purely smectic where all the members exhibit enantiotropic smectic mesophases. Re-entrant nematic phase is absent in both the series.

Both the series exhibit the normal odd-even effect. The even members occupy the upper curve as for the nematic-isotropic transitions.

The group efficiency order obtained for the smectic mesophase in the homologous series (5 to 8) is extended for these two smectogenic series and can be represented as under :

$NO_2 > CN > OH > OC_4H_9 > C_4H_9 > C_2H_5 \approx CH_3 > OC_2H_5 > H > OCH_3$

Gray (74) has derived group efficiency order for promoting smectic and nematic phases in biphenyl and p-amino cinnamate Schiff base compounds. In the smectic group efficiency order derived by Gray (74), the $-NO_2$ and -CN groups are at the bottom whereas in the present study they are at the top. This suggests that the different attractive forces operating in series 9 and 10 having -CN and $-NO_2$ are quite opposite than those operating in the systems reported by Gray (74).

C. Mesogenic Mixtures

System I, II and III exhibit nematic mesophase in all the compositions. System I and II are simple eutectic type. The nematic mesophase in system I remains monotropic in all the composition.

In the system I, a composition with 52 mole percent of A has great supercooling tendency and it exhibits nematic mesophase at room temperature. Nematic mesophase does not crystallize even on supercooling it at 0°C. All the mixtures show marked supercooling tendencies and crystallize well below their mesomorphic temperature. The different composition of system II exhibits monotropic and enantiotropic nematic mesophases.

In the case of system III an advantage is obtained over the individual nematogenic components.

The nematic-isotropic transition temperature curve is a straight line indicating ideal behaviour of the mixtures in mesogenic stage. The solid-nematic transition temperature curve exhibits rounded minimum and a large mesophase range and lowering of the solid-mesomorphic transition temperature is obtained. These mixtures can be more convinient in different studies as they exhibit nematic mesophases at ambient temperatures.