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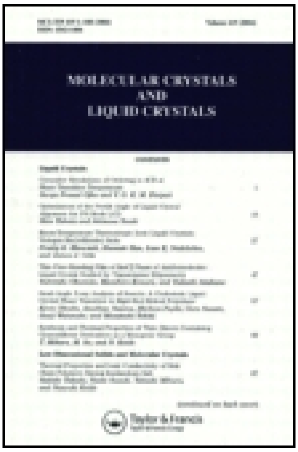

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# Liquid Crystals with Symmetrical Diamide Linkages

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# Liquid Crystals with Symmetrical Diamide Linkages

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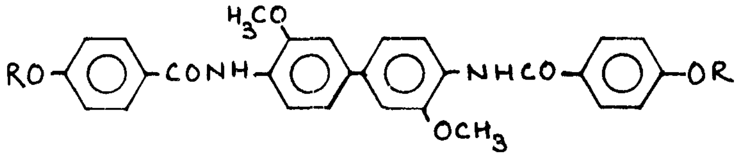
*(Received July 26, 1990)*

The Liquid Crystalline Compounds comprising of amide linkages are rare as it was believed that amide linkages are deterrent to mesomorphism. Our school has contributed significantly in synthesizing and evaluating the mesogenic properties of amide compounds (1, 2, 3). So far compounds with single amide linkage were studied and these were found to be thermally stable Liquid Crystals. In the present study attempt has been made to evaluate the mesogenic properties of compounds with two amido linkages. The two amide linkages will raise the solid-mesomorphic temperature very high, hence two lateral methoxy substituents were preferred on the biphenyl ring to depress the solid-mesomorphic temperatures. The first ever extensive series with diamide linkages behaves like a normal nematogenic series with wide range of mesomorphism. The lower members are nematic, the middle members exhibit polymesomorphism and the higher members exhibit only smectic mesophases. The series is thermally quite stable. The present work is compared with structurally related compounds to evaluate the salient features of the series. The smectic phases are characterized from the textures and by the contact method. The role of acoplanarity in reducing the mesogenic properties is evaluated by spectroscopic measurements of substituted and non-substituted biphenyl derivatives.

*Keywords: diamides, lateral substituent, enhanced smectic phases*

## INTRODUCTION

In recent years Liquid Crystalline Polyamides are becoming commercially important mainly in the field of fibre production. To understand the mesomorphic behaviour of these polymers, it becomes necessary to synthesize some model mesogens and evaluate their mesogenic properties. In our earlier paper[1] series with one amide linkage was synthesized and studied. In the present work mesogens with two amide linkages, without any other central linkage are synthesized (series-I) and studied to evaluate the effect of central amide linkages on mesomorphism.



R = $C_1$ to $C_{18}$ n-alkyl chain.

TABLE I

| | R | Smectic | Transition Temperatures °C<br>Nematic | Isotropic |
|---|---|---|---|---|
| 1. | Methyl | - | 223.0 | 308.0 |
| 2. | Ethyl | - | 235.0 | 321.0 |
| 3. | Propyl | - | 203.0 | 284.0 |
| 4. | Butyl | - | 207.0 | 274.0 |
| 5. | Pentyl | - | 185.0 | 249.0 |
| 6. | Hexyl | - | 190.0 | 241.0 |
| 7. | Heptyl | - | 165.0 | 228.0 |
| 8. | Octyl | - | 171.0 | 210.0 |
| 9. | Decyl | 137.0 | 152.0 | 203.0 |
| 10. | Dodecyl | 128.0 | 171.0 | 184.0 |
| 11. | Tetradecyl | 121.0 | - | 178.0 |
| 12. | Hexadecyl | 118.0 | - | 175.0 |
| 13. | Octadecyl | 118.0 | - | 164.0 |

TABLE II
DSC analysis

| No. of carbon atoms in Alkyl chain R | Phase | Transition Temperatures °C | Enthalpy ΔH J/G | Entropy ΔSJ/G.K. |
|---|---|---|---|---|
| 7 | N | 163.9 | 78.51 | 0.179 |
| | I | 221.9 | 2.056 | 0.0041 |
| 10 | S | 134.4 | 40.13 | 0.098 |
| | N | 150.6 | 0.64 | 0.0015 |
| | I | 196.9 | 2.17 | 0.0046 |
| 14 | S | 122.0 | 59.24 | 0.146 |
| | I | 181.0 | 8.46 | 0.018 |
| 16 | S | 119.5 | 51.39 | 0.131 |
| | I | 176.8 | 7.6 | 0.017 |

IR ANALYSIS

$C_6$ 3350 $cm^{-1}$, 2800 $cm^{-1}$, 1650 $cm^{-1}$, 1600 $cm^{-1}$, 1500 $cm^{-1}$, 1260 $cm^{-1}$.

$C_{16}$ 3450 $cm^{-1}$, 2800 $cm^{-1}$, 1670 $cm^{-1}$, 1600 $cm^{-1}$, 1500 $cm^{-1}$, 1250 $cm^{-1}$.

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## EXPERIMENTAL

The series-I Bis *p,p′*(*p″*-*n*-alkoxy benzanillide)-*o*-dianisidine was synthesized by the following steps.

(i) 4-*n*-alkoxy benzoic acids and 4-*n*-alkoxy benzoyl chlorides were synthesized by the known methods of Dave and Vora.[4]

(ii) Bis *p,p′*(*p″*-*n*-alkoxy benzanillide)-*o*-dianisidines were synthesized by condensing appropriate acid chlorides (0.1 mole) and *o*-dianisidine (0.05 mole) in pyridine.

The reaction mixture was heated for 30 mins. at 70–80°C, and left overnight. The reaction mixture was decomposed in ice cold 1:1 HCl solution, the solid was filtered, washed with saturated $NaHCO_3$ solution, followed by distilled water. The compounds were crystallized from glacial acetic acid till constant transition temperatures are obtained. The transition temperatures are reported in Table I. The compounds are characterized by elemental analysis, Infra red spectroscopy and DSC analysis (Table II).

The transition temperature were determined by using Leitz Laborlux 12 POL microscope.

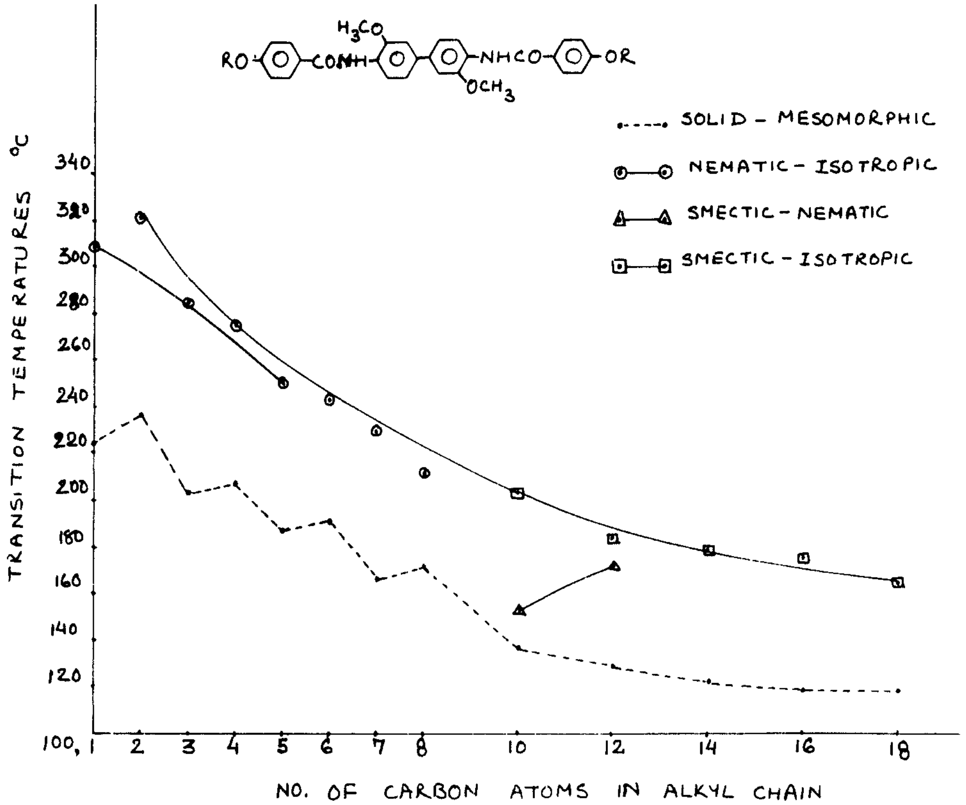

FIGURE 1.

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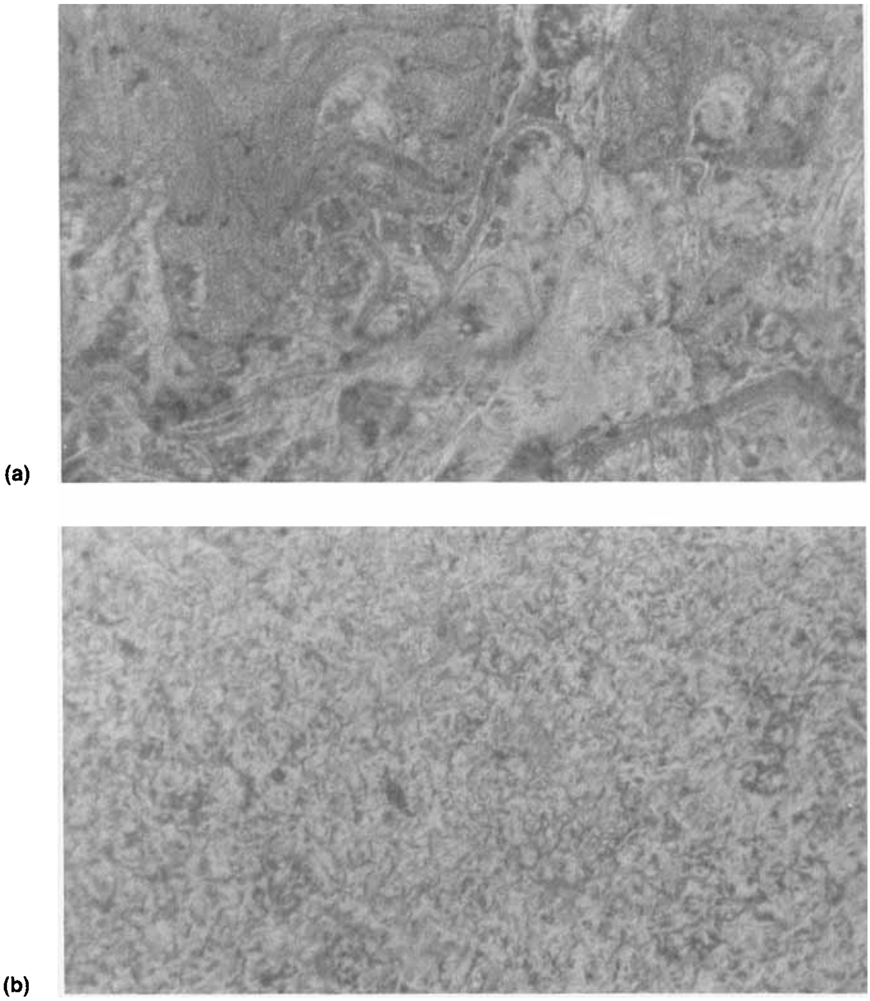

FIGURE 2a and 2b. See Color Plate III.

## CHARACTERIZATION OF SMECTIC PHASES

(a) *Texture*: The optical microscopy indicated that the texture is Schlierin texture exhibited by Smectic C phases. Focal-Conic-fan-shaped texture is not observed in any of the Smectogenic compounds.

(b) *Contact method*: The contact method is considered reliable for the identification of smectic phases. The intermiscibility of smectic phases of homologues was studied. The smectic phases of all the homologues (Decyl to octadecyloxy) are completely miscible indicating exhibition of same type of smectic phase by these homologues.

One of the homologues exhibiting smectic phase was selected for the miscibility

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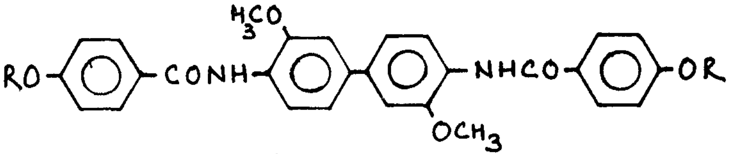
study with labelled C compounds 4-*n*-Octadecyloxy benzoic acid to ascertain further whether the smectic phases are of smectic type or not.

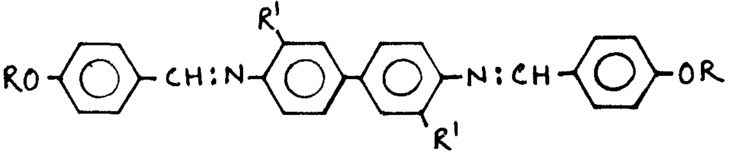
The miscibility studies indicated that the smectic phases exhibited by the homologues of series-I are of smectic-C type (Figures 2(a) and 2(b)).

Methoxy to octyloxy derivatives exhibit only nematic phases. Decyloxy to tetradecyloxy derivatives exhibit smectic-C and nematic phases. Last two members of the series hexadecyloxy and octadecycloxy derivatives exhibit only smectic phases. Normally a homologous series with two lateral methoxy substituents will not exhibit smectic phases as smectic phases are more prone to increase in breadth and acoplanarity.

The comparison with other mesogenic schiff bases with similar structure would be quite interesting. Series II does not exhibit smectic phase (5).



( I )



( II )

R = $-CH_3$, $-C_2H_5$, $-C_{10}H_{21}$;   R' = $-OCH_3$, $-CH_3$

The mesogenic properties of Series-I thus clearly indicates that amide linkages are more conducive to smectic phases though they enhance nematic thermal stabilities compared to schiff base linkages.

The enhanced mesogenic properties are attributed to high polarizability and linearity imparted to the molecules by amide central linkages.

## Acknowledgment

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