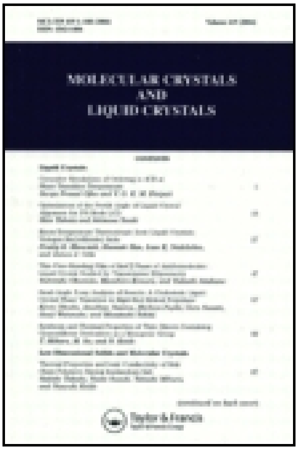

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Homologous Series containing Ester and Amide Groups as Central Linkages: 4(4ˈ-n-Alkoxybenzoyloxy)-4″-n-Heptyloxy Benzanilides

R. A. Vora [a] & Renu Gupta [a]
[a] Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Baroda, 390 001, India

Version of record first published: 14 Oct 2011.

To cite this article: R. A. Vora & Renu Gupta (1981): A Homologous Series containing Ester and Amide Groups as Central Linkages: 4(4ˈ-n-Alkoxybenzoyloxy)-4″-n-Heptyloxy Benzanilides, Molecular Crystals and Liquid Crystals, 67:1, 215-220

To link to this article: http://dx.doi.org/10.1080/00268948108070890

Mol. Cryst. Liq. Cryst., 1981, Vol. 67, pp. 215–220
0026–8941/81/6704–0215$06.50/0

Printed in the U.S.A.

A Homologous Series containing Ester and Amide Groups as Central Linkages: 4(4′-*n*-Alkoxybenzoyloxy)-4″-*n*-Heptyloxy Benzanilides

R. A. VORA and RENU GUPTA

Applied Chemistry Department, Faculty of Technology and Engineering, M.S. University of Baroda, Baroda-390 001, India

(*Received August 5, 1980*)

The first extensive homologous series, comprising thirteen members, with both ester and amide groups as central linkages has been synthesised and the mesomorphic properties have been determined. The homologues are comparatively high melting and exhibit liquid crystal phases. The molecular structure seems to favour smectic properties since smectic phases commence with the ethoxy derivative as a monotropic phase. The ethoxy to hexadecyloxy derivatives are polymesomorphic in nature, while the octadecyloxy derivative is purely smectic. The mesomorphic behaviour and mesophase thermal stabilities are compared with those of other structurally related series, and the effect of the amide group on mesomorphism is evaluated.

INTRODUCTION

The liquid crystalline order in polymers is of great importance and interest since, recently liquid crystalline polymers have acquired technological applications, particularly in the field of fibre production. Many of these polymers incorporate an amide linkage, and model compounds exhibiting mesomorphism and having an amide group may enable us to understand better the mesogenic behaviour of such polymers.

Neither Brown and Shaw[1] in their review on '*The Mesomorphic State*' nor Gray[2] in his classical monograph on liquid crystals has suggested that the amide group would be conducive to mesogenic properties. Recently

---

Paper presented at the 8th International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

Gray[3] has mentioned that the introduction of a group such as —NH—CO— as one of the central linking groups would be detrimental to mesogenic behaviour, compared with the situation where both linking groups are known to be conducive to mesophase formation. This conclusion was based mainly on the presupposition that intermolecular hydrogen bonds would raise the m.p. considerably, rather than that the mesophase thermal stability would be reduced, i.e., the detrimental effect would stem from a narrower mesophase range at a higher temperature, so limiting the usefulness of the material.

To explore the mesogenic characteristics of the amide group, the present homologous series with an amide group as one of the central linkages was synthesised.

EXPERIMENTAL

i) 4-*n-Alkoxybenzoic acids and* 4-*n-Alkoxybenzoyl chlorides*: These were synthesised by methods reported in literature.[4]

ii) 4-*n-Heptyloxy-4′-hydroxybenzanilide*: 4-Aminophenol(0.01 mole) was taken up in dry pyridine (10 ml) and added slowly, with constant stirring, to cold 4-n-heptyloxybenzoyl chloride(0.01 mole). The mixture was heated on a water bath for 1 h and then allowed to stand overnight. It was acidified with cold 1:1 hydrochloric acid, and the precipitate was washed with cold water. Crystallisation from glacial acetic acid gave a yield of about 50%. The melting point of the compound is 198°C.

iii) 4(4′-*n-Alkoxybenzoyloxy*)-4″-*n-heptyloxybenzanilides* 4-n-Heptyloxy-4′-hydroxybenzanilide(0.01 mole), taken up in dry pyridine (10 ml), was slowly added to cold 4-n-alkoxybenzoyl chloride(0.01 mole) and the synthesis was carried out as discussed above. The esters were crystallised from glacial acetic acid until constant transition temperatures were obtained. The transition temperatures are summarised in Table I. The elemental analytical data were satisfactory.

iv) *Determination of Transition Temperatures*: The melting points and transition temperatures were determined using a Mettler FP-52 polarising microscope equipped with a heating stage.

TABLE I

4(4′-n-Alkoxybenzoyloxy)-4″-n-Heptyloxybenzalilides RO-C_6H_4-COO-C_6H_4-HNCO-C_6H_4-OC_7H_{15}

Compound No	n-Alkyl group R	Transition (C − S/N)	Temperatures (S − N)	(°C) (N or S − I)
1	Methyl	194.0	—	239.5
2	Ethyl	180.0	(178.0)	238.5
3	Propyl	187.0	(184.5)	235.0
4	Butyl	198.0	199.0	237.0
5	Pentyl	198.0	202.0	230.0
6	Hexyl	194.5	209.0	226.0
7	Heptyl	190.0	211.0	222.5
8	Octyl	188.0	217.0	226.0
9	Decyl	176.0	216.5	221.5
10	Dodecyl	179.0	213.0	217.5
11	Tetradecyl	171.0	210.0	215.0
12	Hexadecyl	166.5	205.5	210.0
13	Octadecyl	168.5	—	208.0

( ) indicates a monotropic S − N transition temperature.

DISCUSSION

The methoxy derivative exhibits only a nematic phase, but smectic mesophases commence with the ethoxy derivative which exhibits a monotropic phase. Polymesomorphism is observed from the ethoxy to the hexadecyloxy derivative, whilst the octadecyloxy derivative exhibits only a smectic mesophase. Though the members of the series have comparatively high melting points, no decomposition is observed on heating.

The plot of transition temperatures against the number of carbon atoms in the alkoxy chain (Figure 1) exhibits the odd–even effect for both the nematic–isotropic and smectic–nematic transition temperatures. The very early commencement of smectic properties in the series probably gives rise to the alternation in the smectic–nematic transition temperatures.

The present series (A) is compared with other structurally related homologous series and the effect of the amide group as a middle linkage is evaluated.

Table II summarises the average nematic and smectic thermal stabilities and the points of commencement of the smectic mesophase in the following series.

i) 4(4′-n-Alkoxybenzoyloxy)-4″-n-heptyloxybenzanilides (A)
ii) 4(4′-n-Alkoxybenzoyloxy)benzylidene-4″-isopentyloxyanilines[5] (B)
iii) 4(4′-n-Alkoxybenzoyloxy)-4″-n-heptyloxyphenyl benzoates.[6] (C)

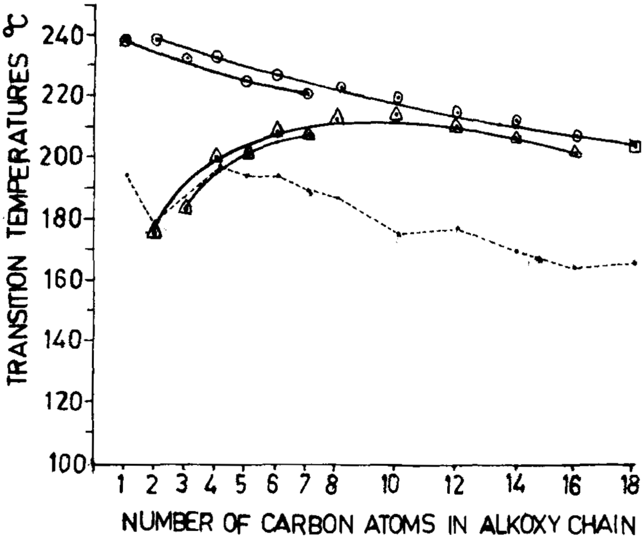

FIGURE 1 ●– – –● Solid to Mesomorphic or Isotropic Liquid,
⊕——⊕ Nematic to Isotropic Liquid,
△——△ Smectic to Nematic,
☐ Smectic to Isotropic Liquid.

The molecular geometry of these series is given in Figure 2.

Reference to Table II indicates that the nematic thermal stabilities of series (B) are almost equal to those of series (A), but the smectic thermal stabilities are much lower (52.5°C). Both series (A) and (B) have ester linkages in common, and the difference lies in the second middle linkage—an amide and an azomethine linkage respectively. However, another major difference lies in the branched terminal alkyl chain in series (B), and this makes strict comparisons between the two series impossible. For example, it might be

TABLE II

Average thermal stabilities

Series	A	B	C
Smectic-Nematic or Isotropic	204.5°	151.0°	110.0°
Nematic-Isotropic	226.5°	225.1°	217.5°

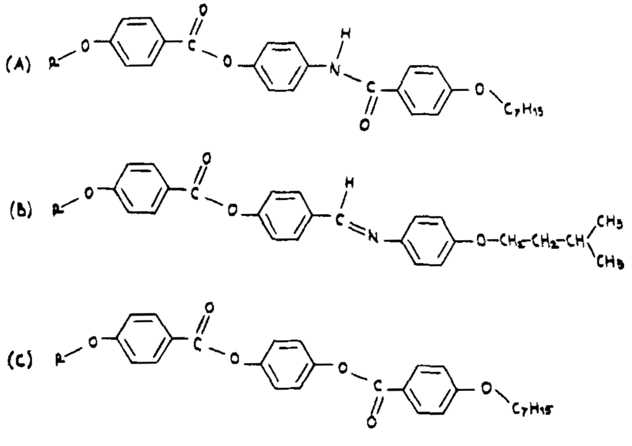

FIGURE 2 Geometry of different series.

concluded that the higher smectic tendencies of series (A) arise from the possibility of intermolecular hydrogen bonding (IR freq. 3340 cm^{-1}) in this series, as suggested in Figure 3. However, the branching in the isopentyloxy chain at the fourth carbon would in itself adversely affect the smectic thermal stabilities of series (B). Conversely, of course, the nematic thermal stabilities of series (B) would also be diminished by the chain branching, and this implies that the amide linkage in series (A) *promotes* the nematic thermal stabilities more than the azomethine linkage in series (B).

The molecules in series (C) and (A) now have same end groups, (see Figure

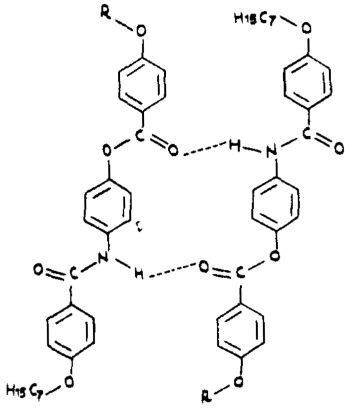

FIGURE 3 Probable arrangement of molecules with intermolecular hydrogen-bonding.

2), and the difference lies only in one central linkage—amide or ester. Here also the difference in the smectic thermal stabilities is much more pronounced than that in the nematic thermal stabilities. We can now conclude that the high lateral attractive forces due to the intermolecular hydrogen bonding are probably responsible for the highly stable smectic mesophases of series (A), and that the amide linking group also promotes nematic thermal stabilities to a somewhat greater extent than the ester linking group.

To summarise the situation, the properties of series (A) suggest that the linearity of the molecules, the high anisotropy of the $—C_6H_4—CO—NH—C_6H_4—$ system,[7] and intermolecular hydrogen bonding confer high nematic and particularly smectic thermal stabilities on the system.

Acknowledgements

The authors are thankful to Prof. Suresh Sethna and Prof. S. M. Sen for their keen interest in the work. They are also indebted to the Head of the Applied Chemistry Department for providing research facilities. One of us (Renu Gupta) is grateful to the University Grant Commission, India, for providing a research grant.

References

1. G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1052 (1957).
2. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals*, Academic Press, London (1962), p. 161.
3. G. W. Gray, *Liquid Crystals and Plastic Crystals*, Vol. 1 (eds. G. W. Gray and P. A. Winsor), Ellis Horwood Ltd., Chichester, England (1974), p. 111.
4. J. S. Dave and R. A. Vora, *Liquid Crystals and Ordered Fluids*, (eds. J. F. Johnson and R. S. Porter), Plenum Press, New York (1970), p. 477.
5. R. A. Vora and N. Dixit, presented at the Annual Convention of Chemists, Kurukshetra, India, 1979.
6. J. P. Van Meter and B. H. Klanderman, *Mol. Cryst. Liq. Cryst.*, **22**, 285 (1973).
7. *Liquid Crystalline Order in Polymers*, (ed. A. Blumstein), Academic Press, New York (1978), p. 52.