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

Mesogens having positive dielectric anisotropy—II: 4(4'-n-Alkoxy-benzoyloxy)-2-methyl-2″-chloro-4″-nitroazobenzenes

R. A. Vora [a] & Nilesh Dixit [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 & Nilesh Dixit (1981): Mesogens having positive dielectric anisotropy—II: 4(4'-n-Alkoxy-benzoyloxy)-2-methyl-2″-chloro-4″-nitroazobenzenes, Molecular Crystals and Liquid Crystals, 67:1, 193-198

To link to this article: http://dx.doi.org/10.1080/00268948108070887

Mol. Cryst. Liq. Cryst., 1981, Vol. 67, pp. 193–198
0026–8941/81/6704–0193$06.50/0

Printed in the U.S.A.

Mesogens having positive dielectric anisotropy—II: 4(4′-*n*-Alkoxy-benzoyloxy)-2-methyl-2″-chloro-4″-nitroazobenzenes

R. A. VORA and NILESH DIXIT

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

(*Received August 18, 1980*)

A homologous series of mesogenic azo-esters having a terminal nitro substituent and methyl and chloro lateral substituents has been synthesized; the mesogenic behaviour of the series has been characterized. All the compounds are red, stable, and should have large positive dielectric anisotropies as the dipole-moment of the terminal nitro group is acting along the long axes of the molecules. The first member is non-mesogenic; the ethoxy to tetradecyloxy derivatives exhibit only nematic mesophases; the hexadecyloxy derivative exhibits smectic and nematic mesophases. The lateral substituents lower the crystal-mesophase and mesophase-isotropic transition temperatures.

INTRODUCTION

The use of liquid crystals in electro-optical display devices has led to a great upsurge in the synthesis of new mesogens, especially those exhibiting mesomorphic properties at room temperature. The search for low melting mesogens revealed that a number of factors influences their melting characteristics. One of these factors is the introduction of a lateral substituent which brings down the crystal-mesophase as well as the mesophase-isotropic transition temperatures.[1,2] Moreover, the preference for mesogens having a positive dielectric anisotropy over those exhibiting negative dielectric anisotropy in optical displays gave impetus to the synthesis of new mesogens with positive dielectric anisotropy.[3–6] In continuation of our work[7] on the

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

synthesis of mesogens with positive dielectric anisotropy and keeping in view the effects of lateral substituents on crystal-mesophase transition temperatures, in the present study we have synthesized a homologous series 4(4′-*n*-alkoxybenzoyloxy)-2-methyl-2″chloro-4″-nitroazobenzenes having methyl and chloro lateral substituents and two central linking groups.

RESULTS AND DISCUSSION

Thirteen members of the series were synthesized and their mesomorphic properties determined. The transition temperatures are summarized in Table I.

The first member is non-mesogenic, the ethoxy to tetradecyloxy members exhibit only nematic mesophases, and the hexadecyloxy member exhibits a nematic as well as a smectic mesophase, but this smectic mesophase is monotropic. The plot of the transition temperatures against the number of carbon atoms in the alkyl chain, for the nematic-isotropic transition temperatures, exhibits the usual odd-even effect, with the even members constituting the upper curve (Figure 1).

Most members of the series melt around 90° to 120° to give mesophases, and exhibit broad nematic mesophase ranges (50–60°). It has been recently observed that the presence of an NO_2 end group in place of other alkoxy groups renders the whole homologous series smectogenic.[8] However, there

TABLE I

4(4′-n-alkoxybenzoyloxy)-2-methyl-2′-chloro-4″-nitroazobenzenes

	Transition temperatures (°C)		
R	Smectic	Nematic	Isotropic
Methyl	—	—	210.0
Ethyl	—	190.0	194.0
Propyl	—	147.0	181.0
Butyl	—	116.0	175.5
Pentyl	—	119.0	162.0
Hexyl	—	118.0	157·0
Heptyl	—	96.0	145.5
Octyl	—	99.0	145.0
Nonyl	—	97.0	138.0
Decyl	—	93.0	134.5
Dodecyl	—	94.0	126.0
Tetradecyl	—	93.0	120.0
Hexadecyl	(103.0)[a]	103.5	113.0

[a] Monotropic transition.

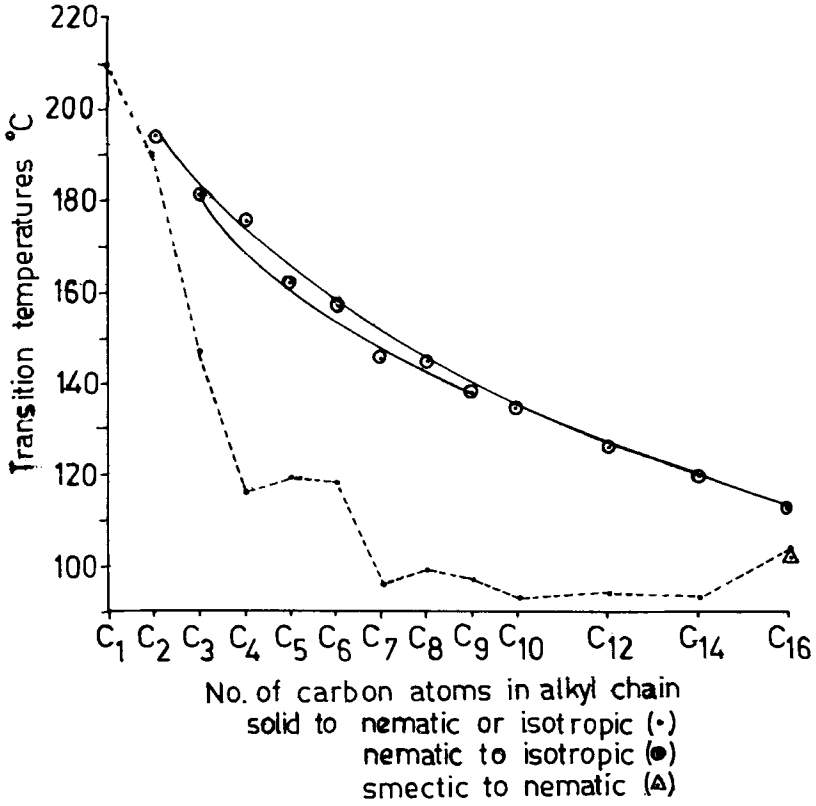

FIGURE 1

are some mesogenic homologous series which exhibit nematogenic behaviour even though the compounds possess an NO_2 end group.[3] Close scrutiny of these series indicates that if the mesogens have a lateral substituent or their geometry is such that even though the NO_2 group is present as an end group, it none the less contributes towards breadth increasing effects, then such series exhibit nematogenic tendencies. If these factors are absent then the NO_2 end group will give a smectogenic series.

Table II summarizes the average thermal stabilities and the points of commencement of smectic mesophase formation for the following series:

A. 4(4′-*n*-alkoxybenzoyloxy)-2-methyl-2″-chloro-4″-nitroazobenzenes.

B. 4-*n*-alkoxy-1-naphthylidene-*p*-aminoazobenzenes.[9]

C. 4-*n*-alkoxybenzylidene-*p*-aminoazobenzenes.[10]

D. 4-(4′-*n*-alkoxybenzoyloxy)-3-methoxybenzylidene-4″-nitroanilines.[11]

TABLE II

Average mesophase thermal stabilities

Series	A	B	C	D
Nematic–Isotropic (°C)	151.0	100.5	170.0	167.0
Smectic–Nematic or Isotropic (°C)	103.0	98.0	151.0	140.0
Commencement of smectic phase	C_{16}	C_{14}	C_4 (C_{16}–C_{18})	C_{10}

Reference to Table II, shows that the smectic thermal stabilities of series A are only a little higher than those of series B. Series A has a nitro end group whereas series B has no such end group. The molecular breadth for series B will be mainly due to the presence of the naphthalene moiety, whereas the two lateral substituents (CH_3 and Cl) present in series A will increase the breadth and acoplanarity of the molecules of series A. It is apparent that the terminal NO_2 group will enhance the mesogenic thermal stabilities of series A, whereas the two lateral substituents will have a depressing effect on both the mesophases. Similarly, the absence of an end group and the breadth increasing effect of the naphthalene moiety should decrease both the mesophase thermal stabilities of series B. The net result of these factors is that the nematic thermal stability of series A is higher than that of series B, whereas the smectic thermal stabilities of both series are almost equal. This is probably because of the greater effect of the two lateral substituents in depressing the thermal stabilities of the smectic mesophases compared with the nematic mesophases in series A; breadth increases are known to have more pronounced effects on smectic mesophases than on nematic mesophases.

The smectic and nematic thermal stabilities of series A are lower than those of series C and D. The molecules of series C have no end group; hence they are shorter in length and less polar compared with those of series A. However, the molecules of series A are broad and more acoplanar, and due to this it is natural that their thermal stabilities would be lower compared with those of series C. It is interesting to note that the difference in average nematic thermal stability between series A and C is only 19°, whereas the difference in smectic thermal stability is 48°. This degree of difference in decrease or increase in smectic and nematic thermal stabilities is normally attributed to the increase or decrease in breadth or thickness of the molecules involved, because breadth changes have more pronounced effects on smectic thermal stabilities compared with nematic thermal stabilities. This explains the observed difference in the decreases in thermal stabilities.

In the case of series D, the difference is in the lateral substituent and in one of the central linkages. Even though the molecules of series D have a bulky

OCH_3 group as the lateral substituent, the depressing effect of the two lateral substituents in series A is more on both the mesophases. This explains the overall lower thermal stabilities of series A compared with those of series D. The difference in the decreases in the thermal stabilities has the same trend as that mentioned above and the explanation is also the same.

The smectic mesophase commences very early in the case of series C, and this is attributed to the high length to breadth ratio. In the case of the other series, the commencement of the smectic mesophase is delayed as the breadth of the molecules is considerably increased.

As the dipole moment of the NO_2 substituent acts along the long axes of the molecules, the members of series A would be expected to exhibit positive dielectric anisotropy.

EXPERIMENTAL

i) *Preparation of p-n-alkoxybenzoic acids*: *p*-n-Alkoxybenzoic acids were synthesized as described by Dave and Vora.[12]

ii) *Preparation of 4-hydroxy-2-methyl-2′-chloro-4′-nitroazobenzene*: 4-Nitro-2-chloroaniline precipitate was filtered off and washed with water. It was then dried and crystallized from ethanol. The yield was 78%.

iii) *Preparation of 4(4′-n-alkoxybenzoyloxy)-2-methyl-2″-chloro-4″-nitrobenzene*: *p*-n-Alkoxybenzoyl chlorides were prepared in the usual way by treating the corresponding acids with an excess of thionyl chloride. The excess of thionyl chloride was distilled off under reduced pressure and the residual acid chlorides were used without purification.

4-Hydroxy-2-methyl-2′-chloro-4′-nitroazobenzene (0.01 mole) was dissolved in dry pyridine (A.R., 10 ml) and the *p*-n-alkoxybenzoyl chloride (0.015 mole) was added slowly with stirring. The mixture was warmed with stirring for one hour and then allowed to stand overnight. After acidification of the mixture with cold, dilute hydrochloric acid, the precipitate was collected by filtration and washed with cold dilute sodium hydroxide solution, followed by water. The solid esters were crystallized from ethyl acetate until constant transition temperatures were obtained.

Determination of transition temperatures

The transition temperatures were determined by using a polarizing microscope in conjunction with a Mettler FP-52 heating stage. The transition temperatures are recorded in Table 1.

Acknowledgements

The authors thank Prof. Suresh Sethna and Prof. S. M. Sen for their keen interest in the work, and the Head of the Department for providing research facilities. One of us (ND) is indebted to CSIR for providing a research grant.

References

1. S. L. Arora, J. L. Fergason, and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **10**, 243 (1970).
2. Z. G. Gardlund, R. J. Curtis, and G. W. Smith, *Liquid Crystals and Ordered Fluids* (Eds. J. F. Johnson and R. S. Porter), Plenum Press, New York (1974), Vol. 2, p. 541.
3. G. W. Gray, *J. Phys.* (*Paris*), **36**, 337 (1975).
4. J. Billard, J. C. Duboid, and A. Zann, *J. Phys.* (*Paris*), **36**, 355 (1975).
5. B. K. Shadashiva, *Mol. Cryst. Liq. Cryst.*, **35**, 205 (1976).
6. G. W. Gray, K. J. Harrison, and A. Nash, *Electron Lett.*, **9**, 130 (1973).
7. R. A. Vora and N. Dixit, *Presented at the International Liquid Crystal Conference, Bangalore, India*, (1979).
8. N. R. Patel, Ph.D. Thesis, M.S. University of Baroda, Baroda, India, (1980).
9. J. S. Dave and A. P. Prajapati, *Pramana*, **1**, 435 (1975).
10. S. L. Arora and J. L. Fergason, *Symposium. Faraday Soc.* No. **5**, p. 97 (1971).
11. R. Gupta, Ph.D. Thesis, M.S. University of Baroda, Baroda, India, (1980).
12. 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.