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

Synthesis and Miscibility Studies of Some Phenyl Cinnamoyloxybenzoate derivatives?

M. Subramanya Raj Urs [a] , B. K. Sadashiva [a] , K. A. Suresh [a] & S. Krishna Prasad [a]
[a] Raman Research Institute, Bangalore, 560080, India

Version of record first published: 13 Dec 2006.

To cite this article: M. Subramanya Raj Urs , B. K. Sadashiva , K. A. Suresh & S. Krishna Prasad (1983): Synthesis and Miscibility Studies of Some Phenyl Cinnamoyloxybenzoate derivatives?, Molecular Crystals and Liquid Crystals, 103:1-4, 235-241

To link to this article: http://dx.doi.org/10.1080/00268948308071055

Mol. Cryst. Liq. Cryst., 1983, Vol. 103, pp. 235–241
0026-8941/83/1034-0235/$18.50/0

Synthesis and Miscibility Studies of Some Phenyl Cinnamoyloxybenzoate derivatives†

M. SUBRAMANYA RAJ URS, B. K. SADASHIVA, K. A. SURESH and S. KRISHNA PRASAD

Raman Research Institute, Bangalore 560080, India

(*Received May 10, 1983*)

Some members of the homologous series, 4-cyanophenyl-3′-methyl-4′(4″-*n*-alkyloxycinnamoyloxy) benzoate and 4-cyanophenyl-3′-methyl-4′(4″-*n*-alkyloxy-α-methyl cinnamoyloxy)benzoate have been prepared. The transitions were studied by hot stage microscopy and differential scanning calorimetry. The undecyloxy- and dodecyloxy-derivatives exhibit a reentrant nematic phase at atmospheric pressure. The effect of a lateral substituent on the reentrant phenomenon in these compounds is discussed.

A detailed study of the phase diagrams of binary mixtures of each of these compounds exhibiting a reentrant phase with 4-cyanophenyl-3′-methyl-4′(4″-*n*-decylbenzoyloxy)benzoate, a compound exhibiting no reentrant phase has been carried out. Interestingly, in three cases, the binary mixtures exhibit stable enantiotropic reentrant behaviour over a range of composition though the pure compounds themselves are monotropic reentrants.

INTRODUCTION

During the last few years, a large number of terminally substituted cyano compounds exhibiting reentrant nematic and smectic A phases at atmospheric pressure have been synthesized.[1-10] However, there has been only one example of a laterally substituted series of compounds exhibiting the reentrant phenomenon.[1] In order to have a better understanding of the effect of lateral substituents on the reentrant

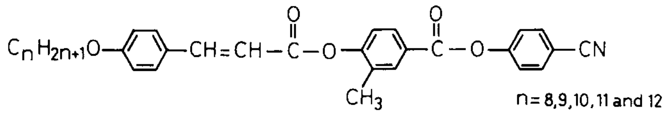
---

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 1982.

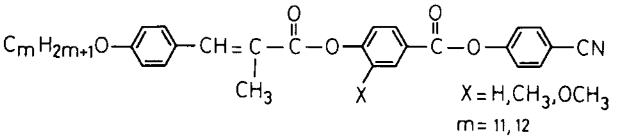
behaviour, we have prepared a number of phenyl-4-cinnamoyloxy benzoate derivatives with lateral methyl and methoxy substituents. In this paper, we discuss the influence of the above lateral substituents on the reentrant phenomenon for which preliminary results have already been published.[11] We have also studied the phase diagrams of binary mixtures of each of these newly synthesized reentrant compounds with 4-cyanophenyl-3′-methyl-4′(4″-*n*-decylbenzoyloxy)benzoate (10 CPMBB), a compound which does not exhibit a reentrant phase.

EXPERIMENTAL

The compounds synthesized have the following structural formulae.



I



II

These compounds were prepared by a procedure similar to the one which has already been described in the literature.[11] The mesophases and transition temperatures were observed by means of a polarizing microscope equipped with a heating and cooling stage (Mettler FP5). These were checked using a differential scanning calorimeter (Perkin–Elmer DSC-2).

RESULTS AND DISCUSSION

The transition temperatures of the compounds of series I and II are given in Tables I and II respectively. In the series 4-cyanophenyl-3′-methyl-4′(4″-*n*-alkyloxycinnamoyloxy)benzoates, compound 4 exhibits a stable reentrant nematic phase while compound 5 shows only a

TABLE I

Transition temperatures (°C) of the compounds with the general formula I

No.	n	K		N_{re}		S_A		N		I
1	8	·	124.4	—		—		·	211.5	·
2	9	·	117.6	—		—		·	205.4	·
3	10	·	97	—		—		·	201	·
4	11	·	102.4	·	107	·	153.2	·	193.6	·
5	12	·	88.5	·	(61)	·	175.3	·	191.7	·

A point (·) implies that the phase is observed and a dash (—) that it is not. Temperature in parenthesis indicate monotropic transition.

TABLE II

Transition temperatures (°C) of the compounds with the general formula II

No.	n	X	K		N_{re}		S_A		N		I
6	11	H	·	95	—		·	197	·	202.7	·
7	12	H	·	94.2	—		·	199	·	200.2	·
8	11	CH_3	·	80.8	·	93	·	122.5	·	169.8	·
9	12	CH_3	·	80	·	(69)	·	149.2	·	165.6	·
10	11	OCH_3	·	82.9	·	(48)	·	123	·	139.8	·
11	12	OCH_3	·	79.5	·	(45)	·	133.2	·	136.4	·

A point (·) implies that the phase is observed and a dash (—) that it is not. Temperature in parenthesis indicate monotropic transition.

monotropic reentrant nematic phase. The lower homologues in this series exhibit only nematic phase. In the case of compounds of series II, compound 8 exhibits a stable reentrant nematic phase while compounds 9, 10 and 11 show only a metastable reentrant nematic phase. A comparison of the two series of compounds clearly establish that the α-methyl substituent has no influence on the reentrant phenomenon. This is perhaps due to the fact that the α-methyl group does not enhance the breadth of the molecule. However, a clear reduction in the melting points as well as the nematic-isotropic transition temperatures in compounds 8 and 9 may be clearly seen. This may be attributed to a thickening effect discussed elsewhere.[12]

The lateral methoxy substituent in compound 10 destabilizes the enantiotropic reentrant nematic phase observed in compound 8 having a smaller lateral methyl substituent. Although the methoxy group has a greater ability to transfer electrons through resonance than the methyl group, it increases the breadth of the molecule considerably. This is reflected in all the transition temperatures of compounds 10 and 11 as compared with compounds 8 and 9. Therefore, there appears to be a balance between the length, breadth and the electron distribution in a terminally cyano substituted compound for the existence of a reentrant phase.

We have carried out, detailed studies on the phase diagrams of binary mixtures of each of these newly synthesized reentrant compounds. The phase diagram of the mixtures of compound 4 and 10 CPMBB is shown in Figure 1. In the pure state compound 4 shows the nematic (N) and smectic A (S_A) phases as well as an enantiotropic reentrant nematic (N_{re}) phase. 10 CPMBB in the pure state shows only the N phase. The mixture shows the N_{re} phase for weight percentages in the range of 0–60 of 10 CPMBB. In the mixture, the range of the N_{re} phase increases with increase in the concentration of 10 CPMBB. For instance, in the mixture of 60 weight per cent of 10 CPMBB in compound 4, the N_{re} phase has a range of about 25 °C though in pure compound 4, the N_{re} phase has a range only of about 4 °C.

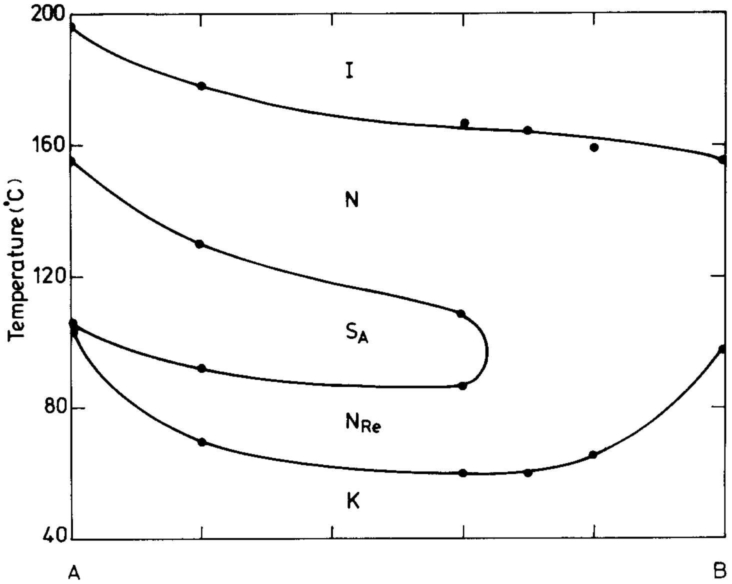


FIGURE 1 Binary phase diagram of a mixture of A: 4-cyanophenyl-3′-methyl-4′(4″-*n*-undecyloxycinnamoyloxy)benzoate; B: 4-cyanophenyl-3′-methyl-4′(4″-*n*-decylbenzoyloxy)benzoate.

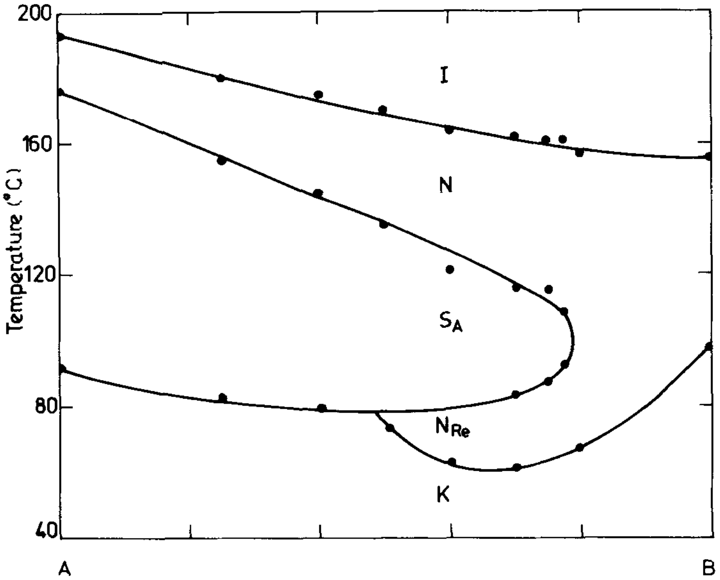


FIGURE 2 Binary phase diagram of a mixture of A: 4-cyanophenyl-3′-methyl-4′(4″-*n*-dodecyloxycinnamoyloxy)benzoate; B: 4-cyanophenyl-3′-methyl-4′(4″-*n*-decylbenzoyloxy)benzoate.

Figure 2 shows the phase diagram of the mixtures of compound 5 and 10 CPMBB. Pure compound 5 shows a N phase, a S_A phase and a monotropic N_{re} phase. The mixture shows the enantiotropic N_{re} phase for weight percentages in the range of about 50–80 of 10 CPMBB.

The phase diagram of mixtures of compound 8 and 10 CPMBB is shown in Figure 3. Compound 8 shows a N phase, a S_A phase and a monotropic N_{re} phase. In this case, the addition of even a very small quantity of 10 CPMBB, changes the monotropic N_{re} phase to an enantiotropic N_{re} phase. Increase in concentration of 10 CPMBB increases the range of the enantiotropic N_{re} phase. The mixture shows the enantiotropic N_{re} phase for weight percentages in the range of about 0–50 of 10 CPMBB.

Figure 4 shows the phase diagram of the mixtures of compound 10 and 10 CPMBB. In the pure state, compound 10 shows a N phase, a S_A phase and a monotropic N_{re} phase. The mixture shows an enantiotropic N_{re} phase for weight percentages in the range of about 25–55 of 10 CPMBB.

Our miscibility studies establish that the lower temperature phase of these newly synthesized compounds are N_{re}. The addition of 10

CPMBB to these compounds stabilizes the N_{re} phase. Interestingly, in three cases, viz., (i) compound 5 and 10 CPMBB, (ii) compound 9 and 10 CPMBB, and (iii) compound 11 and 10 CPMBB, the binary mixtures exhibit stable enantiotropic reentrant behaviour over a range of compositions though the pure reentrant compounds themselves are only monotropic.

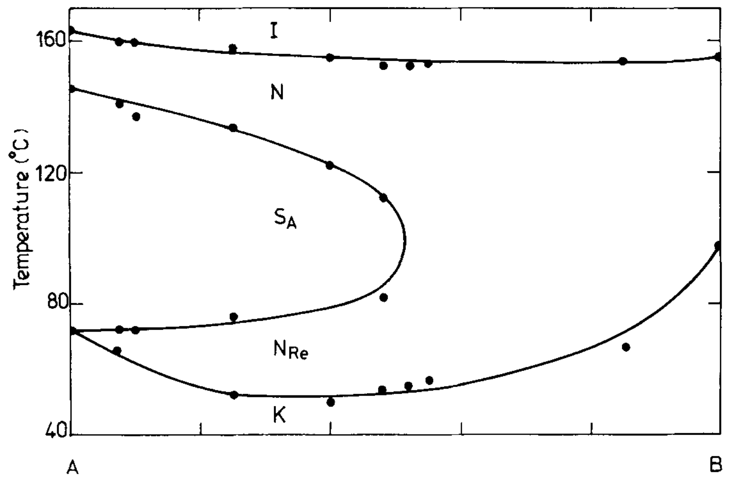


FIGURE 3 Binary phase diagram of a mixture of A: 4-cyanophenyl-3′-methyl-4′(4″-*n*-dodecyloxy α-methylcinnamoyloxy)benzoate; B: 4-cyanophenyl-3′-methyl-4′(4″-*n*-decylbenzoyloxy)benzoate.

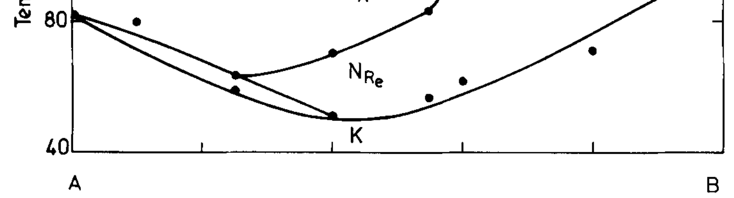


FIGURE 4 Binary phase diagram of a mixture of A: 4-cyanophenyl-3′-methoxy-4′(4″-*n*-undecyloxy α-methylcinnamoyloxy)benzoate; B: 4-cyanophenyl-3′-methyl-4′(4″-*n*-decylbenzoyloxy)benzoate.

Further work is in progress to study the effect of the lateral substituents on the reentrant phenomenon.

Acknowledgments

We are grateful to Professor S. Chandrasekhar and Dr. N. V. Madhusudana for many useful suggestions.

References

1. F. Hardouin, G. Sigaud, M. F. Achard and H. Gasparoux, *Phys. Lett.*, **71A**, 347 (1979).
2. N. V. Madhusudana, B. K. Sadashiva and K. P. L. Moodithaya, *Current Science*, **48**, 613 (1979).
3. Nguyen Huu Tinh and H. Gasparoux, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 287 (1979).
4. F. Hardouin, A. M. Levelut, Nguyen Huu Tinh and G. Sigaud, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 35 (1979).
5. B. K. Sadashiva, *Proceedings of the International Liquid Crystals Conf.*, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London (1980) p. 165.
6. Nguyen Huu Tinh, M. Joussot-Dubien, C. Destrade, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 257 (1980).
7. D. Demus, G. Pelzl, A. Wiegeleben and W. Weissflog, P *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 289 (1980).
8. W. Weissflog, G. Pelzl, A. Wiegeleben and D. Demus, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 295 (1980).
9. Nguyen Huu Tinh, A. Pourrere and C. Destrade, *Mol. Cryst. Liq. Cryst.*, **62**, 125 (1980).
10. Nguyen Huu Tinh, A. Zann, J. C. Dubois and J. Billard, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 323 (1980).
11. M. Subramanya Raj Urs and B. K. Sadashiva, *Mol. Cryst. Liq. Cryst. Lett.*, **72**, 227 (1982).
12. B. K. Sadashiva, *Mol. Cryst. Liq. Cryst.*, **35**, 205 (1976).