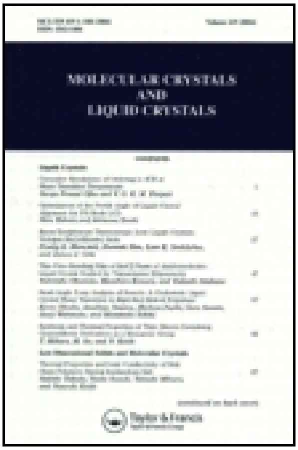


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Phenyl-4-benzoyloxybenzoates with Lateral Methoxy Substituent

M. Subramanya Raj Urs [a] & V. Surendranath [a]
[a] Raman Research Institute, Bangalore, 560080, India

Version of record first published: 17 Oct 2011.

To cite this article: M. Subramanya Raj Urs & V. Surendranath (1983): Phenyl-4-benzoyloxybenzoates with Lateral Methoxy Substituent, Molecular Crystals and Liquid Crystals, 99:1, 279-284

To link to this article: http://dx.doi.org/10.1080/00268948308072049

Mol. Cryst. Liq. Cryst., 1983, Vol. 99, pp. 279–284
0026-8941/83/9904–0279/$18.50/0

Phenyl-4-benzoyloxybenzoates with Lateral Methoxy Substituent[†]

M. SUBRAMANYA RAJ URS and V. SURENDRANATH

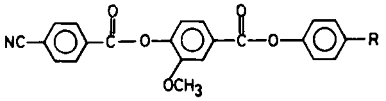
Raman Research Institute, Bangalore 560080, India

(Received February 28, 1983)

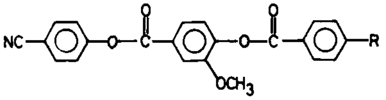
Three new series of compounds exhibiting nematic and smectic A phases have been prepared: 4-*n*-alkyl phenyl-3′-methoxy-4′-(4″-cyanobenzoyloxy) benzoate series, 4-cyanophenyl-3′-methoxy-4′-(4″-*n*-alkyl-benzoyloxy) benzoate series, and 4-*n*- alkylphenyl-3′-methoxy-4′-(4″-bromobenzoyloxy) benzoate series. The influence of lateral methoxy substituent on the mesomorphic properties is discussed.

INTRODUCTION

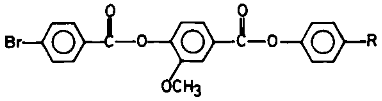
Some phenyl 4-benzoyloxybenzoates with a cyano end group and a lateral methyl group exhibit the reentrant nematic phase.[1] To study the effect of a lateral methoxy substituent on the reentrant behavior, the following series of compountds were synthesized and their mesomorphic properties studied.



I



II

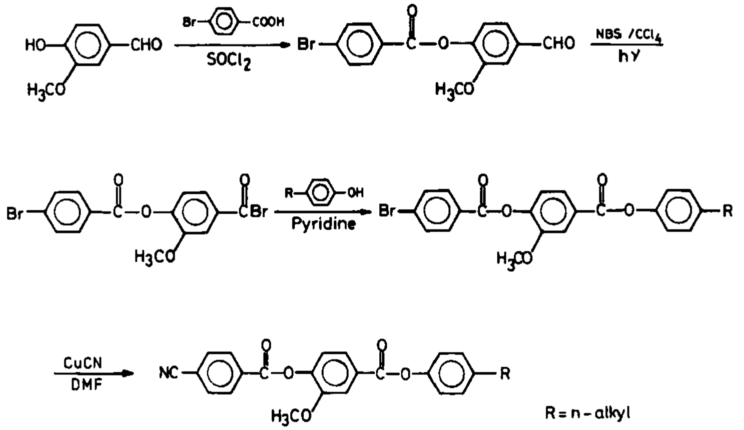


III

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

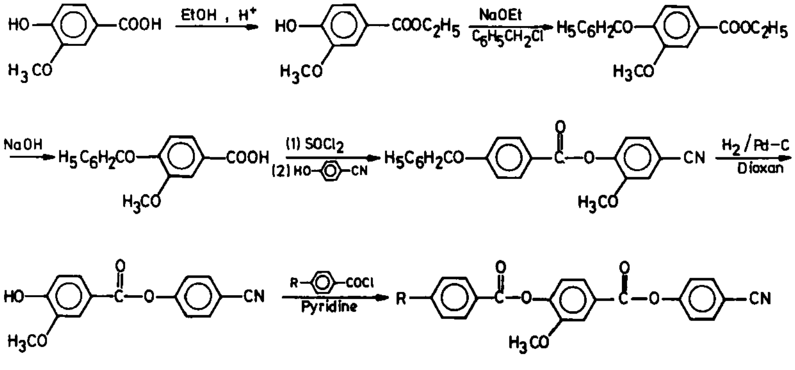
EXPERIMENTAL

The synthesis of the compounds having formula I and III was accomplished according to the following scheme:



An important variation from the usual procedure in the above synthesis is the conversion of the intermediate aldehyde directly to the acid bromide using N-bromo-succinimide. This is an extension of the method used for the preparation of aromatic esters from aromatic aldehydes.[2] In a typical reaction, N-bromosuccinimide (1.1 mol) was added to the solution of aldehyde 2 (10 m.mol) in carbon tetrachloride (20 ml) and the mixture illuminated with 150 W flood lamp. After the completion of the reaction (20 min) succinimide was filtered off and the acid bromide obtained after solvent removal was converted *in situ* to the ester. The esters were obtained in good yields (70–80%). The remaining conversions in the reaction sequence were carried out according to standard methods.

The compounds of the formula II were prepared by standard methods[3] according to the following scheme:



Since the main aim of this work was to study the reentrant mesomorphism, only the eleventh and twelfth members in this series were synthesized and no attempt was made to prepare the lower homologues which are very unlikely to exhibit reentrant mesomorphism.

Each compound was purified by chromatography on silica gel, eluted with a mixture of hexane and benzene (1 : 1) followed by recrystallization from ethanol. The purity of the final product was checked by thin layer chromatogrpahy. All the compounds gave satisfactory elemental analysis. The infrared and nmr spectra were in agreement with their structures. The transition temperatures were determined with a Mettler hot stage (FP-5) in conjunction with a polarizing microscope.

RESULTS AND DISCUSSION

The transition temperatures of compounds having the general formula I, II and III are given in Tables I, II and III, respectively. In the series I all the members exhibit nematic mesophase. The first member is monotropic in nature. The tenth member exhibits a monotropic smectic A phase in addition to an enantiotropic nematic phase. The eleventh and twelfth members exhibit both an enantiotropic smectic A and nematic phases. Figure 1 shows the plot of transition temperatures as a function of the number of carbon atoms in the alkyl chain of 4-*n*-alkyl phenyl-3′-methoxy-4′-(4″-cyanobenzoyloxy)benzoate. The nematic isotropic transition temperatures show the usual odd-even behavior. However, there is no reentrant mesomorphism. The layer spacings for some of the members of the series have

TABLE I

Transition temperatures of 4-*n*-Alkylphenyl-3′-methoxy-4′-(4″-cyanobenzoyloxy)benzoate

n	K		S_A		N		I
1	(•	193)	–		•	194	•
2	•	153	–		•	180	•
3	•	138	–		•	182	•
4	•	126.2	–		•	166.9	•
5	•	130	–		•	167	•
6	•	127.0	–		•	154	•
7	•	106.7	–		•	152	•
8	•	107	–		•	143.8	•
9	•	101.2	–		•	142.0	•
10	•	98.7	(•	94.4)	•	136.1	•
11	•	104.5	•	121.8	•	135.9	•
12	•	101.7	•	130.3	•	133.2	•

( ) Denotes monotropic transition.

TABLE II

Transition temperatures of 4-cyanophenyl-3′-methoxy-4′-(4″-*n*-alkylbenzoyloxy)benzoate

n	K		S_A		N		I
11	•	121.1	•	129.5	•	132.7	•
12	•	123	•		–	132.7	•

TABLE III

Transition temperatures of 4-*n*-alkylphenyl-3′-methoxy-4′-(4″-bromobenzoyloxy)benzoate

n	K		S_A		N		I
1	•		–	(93.4)	•	124.8	•
2	•		–	(82.5)	•	128	•
3	•		–	104.7	•	113.9	•
4	•		–	95.2	•	133.3	•
5	•		–	(109.8)	•	137.2	•
6	•		–	(94.1)	•	102	•
7	•		–	(97.2)	•	101	•
8	•		–	88	•	95.4	•
9	•		–	(96.2)	•	101.3	•
10	•		–	(84)	•	100.9	•
11	•	(85.3)	•	(95.6)	•	102.5	•
12	•	(86.5)	•	(93)	•	94.2	•

( ) Denotes monotropic transition.

been determined by X-ray studies.[4] It is interesting to note that the layer spacing exhibited by the tenth and twelfth members is approximately 1.6 times the molecular length and further it decreases rapidly with the increase of temperature in the smectic A phase.[4] The cyano compounds of series II (eleventh and twelfth members) in which the alkyl and cyano groups are interchanged exhibit only enantiotropic smectic A and nematic phases but no reentrant mesomorphism. As a result of interchanging the alkyl and cyano groups the net dipole moment of the molecule is increased since the dipole moment of ester linkages and the cyano end groups are now acting in the same direction. On the other hand, in the compounds of series I they are acting in opposite directions. It is to be expected that the increase in the dipole moment of the molecule would lead to reentrant mesophase. Indeed, the corresponding compounds with a lateral methyl substituent[1] exhibit a reentrant nematic phase.[1] The absence of reentrant mesophase in series II,

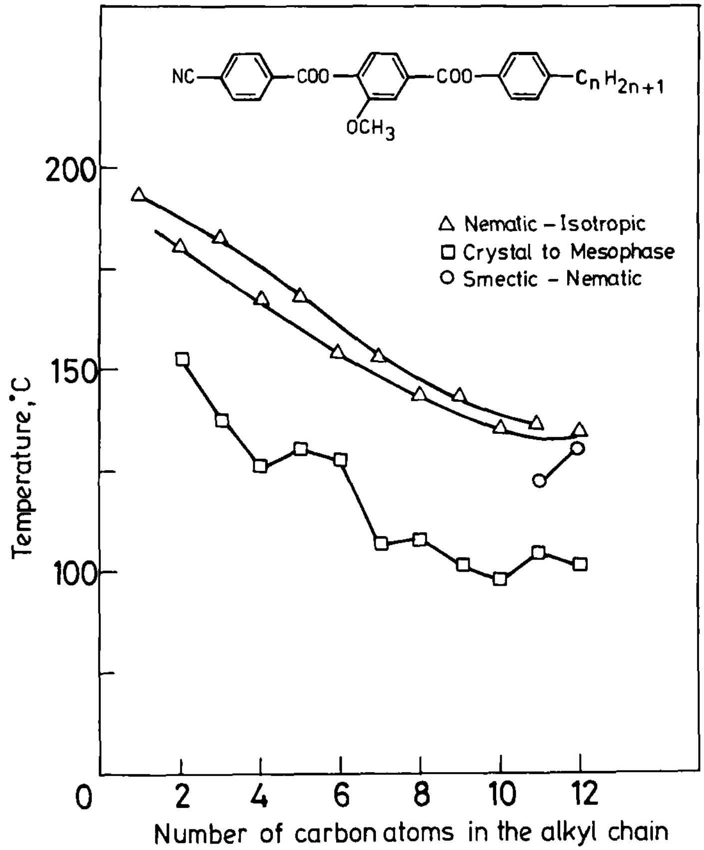


FIGURE 1

contrary to expectations is probably due to the greater size of the lateral methoxy group as compared to that of lateral methyl group. The lateral methoxy group ortho to the ester linkage will have a two fold effect on the the geometry of the molecule. First, it increases the breadth of the molecule and second, it reduces the coplanarity of the molecule. These effects apparently play a decisive role in inhibiting the reentrant mesomorphism.

The bromo compounds of the series III which are precursors to the cyano compounds of series I also exhibit mesomorphism. Most of the members in this series exhibit monotropic nematic phase (Table III). The third, fourth and eighth members show an enantiotropic nematic phase the eleventh and twelfth members manifest a monotropic smectic A phase also.

CONCLUSIONS

The study of the mesomorphic properties of phenyl benzoyloxybenzoates with a lateral methoxy substituent shows that these compounds do not exhibit reentrant mesomorphism. The bulky lateral methoxy group is presumably suppressing the reentrant mesomorphism.

Acknowledgments

We are indebted to Prof. S. Chandrasekhar for many useful discussions and encouragement. We are also thankful to Dr. N. V. Madhusudana for many valuable suggestions and help.

References

1. N. V. Madhusudana, B. K. Sadashiva and K. P. L. Moodithaya, *Curr. Sci.*, **48**, 613 (1979).
2. T. Yak-Fa Cheung, *Tetrahedron Letters*, **40**, 3809 (1979).
3. B. K. Sadashiva, *Mol. Cryst. Liq. Cryst.*, **53**, 253 (1979).
4. N. V. Madhusudana, B. S. Srikanta and M. Subramanya Raj Urs, *Mol. Cryst. Liq. Cryst.* (In Press).