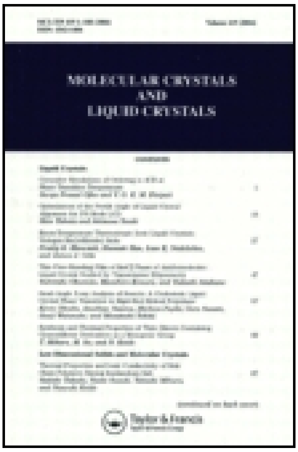


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mesomorphic Properties of Alkoxymethylene-Substituted-Phenyl Esters with Three-Ring Systems

Teruo Kitamura [a], Akio Mukoh [a], Tsunenori Fujii [b] & Kenji Suzuki [b]
[a] Hitachi Research Laboratory, Hitachi Ltd., 4026 Kuji, Hitachi, Ibaraki, Japan, 319-12
[b] Central Research Laboratory, Kanto Chemical Co., Inc., 2048 Inari, Soka, Saitama, Japan, 340

To cite this article: Teruo Kitamura, Akio Mukoh, Tsunenori Fujii & Kenji Suzuki (1987): Mesomorphic Properties of Alkoxymethylene-Substituted-Phenyl Esters with Three-Ring Systems, Molecular Crystals and Liquid Crystals, 149:1, 177-184

To link to this article: http://dx.doi.org/10.1080/00268948708082978

Mol. Cryst. Liq. Cryst., 1987, Vol. 149, pp. 177–184
Photocopying permitted by license only

Printed in the United States of America

Mesomorphic Properties of Alkoxymethylene-Substituted-Phenyl Esters with Three-Ring Systems

TERUO KITAMURA and AKIO MUKOH

Hitachi Research Laboratory, Hitachi Ltd., 4026 Kuji, Hitachi, Ibaraki, Japan 319-12

and

TSUNENORI FUJII and KENJI SUZUKI

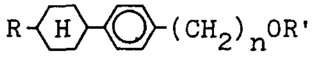
Central Research Laboratory, Kanto Chemical Co., Inc., 2048 Inari, Soka, Saitama, Japan 340

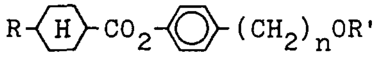
(*Received October 17, 1986; in final form January 20, 1987*)

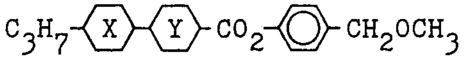
The mesomorphic properties of alkoxymethylene-substituted-phenyl esters with three-ring systems are described. Such ester compounds exhibit enantiotropic nematic and smectic phases. Their clearing points are moderately high, and these transition temperatures are lower than those of alkoxy-substituted esters.

In previous papers,[1,2,3] we reported the nematic properties of new mesogens with alkoxymethylene groups as terminal groups. These compounds were 4-alkoxymethylene-substituted-phenyl 4′-alkylcyclohexanes (I)[1] and 4-alkoxymethylene-substituted-phenyl 4′-alkylcyclohexanecarboxylates (II).[2,3] These species exhibited monotropic nematic or/and smectic phases, and their clearing points are lower than those of alkoxy-substituted compounds. And, as another effect of reduction, the bulk viscosity by alkoxymethylene groups was noticed.

In this paper, alkoxymethylene-substituted-phenyl esters with three-ring systems (III) are synthesized and their mesomorphic properties are examined compared with the corresponding alkoxy- or alkyl-substituted esters.


(I)


(II)


(III)

R,R' = alkyl , n = 1 to5

X , Y = benzene, cyclohexane

The compounds (III) are prepared as shown in Figure 1. The methoxymethyl-substituted-phenol is synthesized by a previously reported[3] procedure. This phenol is esterified with commercial benzoic acid or cyclohexanecarboxylic acid derivatives. Details of the synthetic procedures will be reported elsewhere.

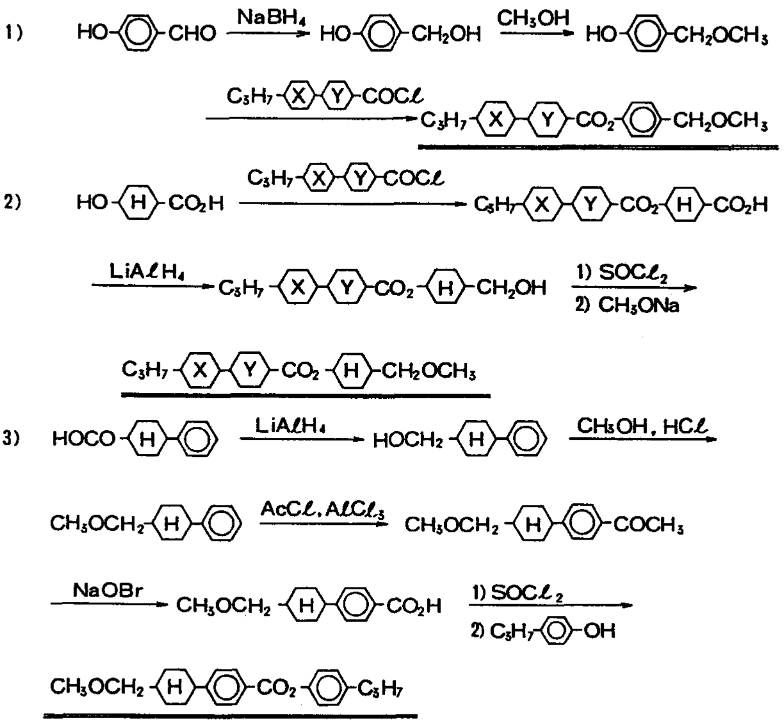
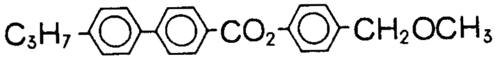
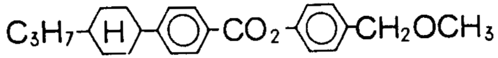
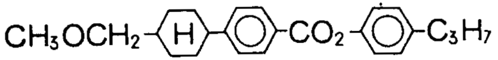
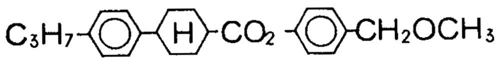
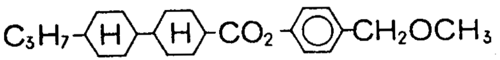
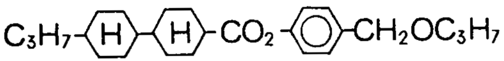
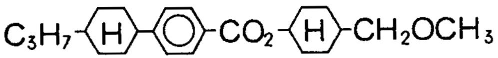
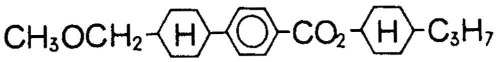


FIGURE 1 Route of synthesis for methoxymethyl-substituted esters. The ring X and Y are benzene or cyclohexane.

TABLE I

Single compounds with their phase transition temperatures in degree centigrade. The abbreviations mean respectively, C; solid phase, S; smectic phase, N; nematic phase, I; isotropic liquid phase. The absence of phase transition is indicated by strokes –.

No.	Structure	Transition Temp. (°C)		
		C–S/N	S–N	N–I
1		103	106	191
2		79	—	131
3		92	105	164
4		87	94	180
5		51	125	131
6		24	130	168
7		92	—	185
8		96	108	145

The phase transition temperatures of the alkoxymethylene series (III) are shown in Table I. Most of these species exhibit enantiotropic nematic and smectic phases, while compounds Nos. 3 and 7 exhibit only nematic phase. In the results on alkoxymethylene-substituted two ring systems (I)[1] and (II),[2,3] tendency to form enantiotropic mesophases of alkoxymethylene series is lower than alkoxy series.[4,5] This is apparently due to the alkoxymethylene groups as terminal groups of mesogens. However, in series (III) as shown in Table I, there is no species which exhibits monotropic mesophases. This may be because the molecular length of three ring systems are longer than series (I), (II) as a hard-rod core. The members of series (III) generally show moderately high clearing points. In particular, the clearing point of compound No. 1 is above 190°C.

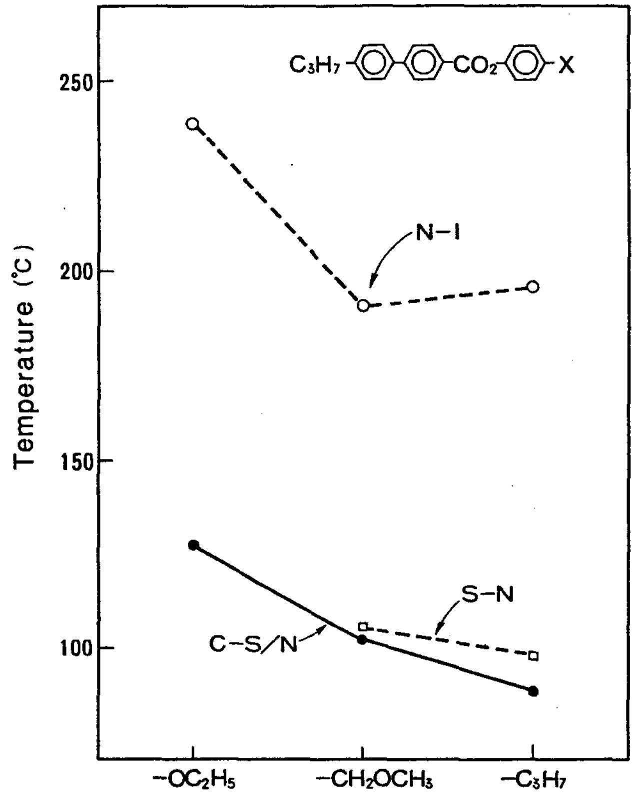


FIGURE 2 Transition temperatures versus substituted groups X, which are ethoxy-, methoxymethyl- and propyl-.

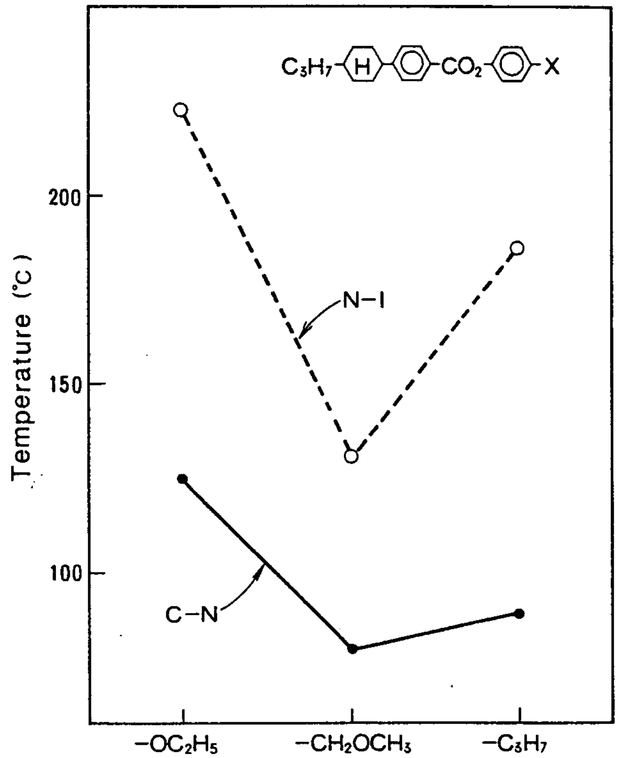


FIGURE 3 Transition temperatures versus substituted groups X, which are ethoxy-, methoxymethyl- and propyl-.

Before going into the discussion on the relationships between transition temperatures and ring systems, we will examine the effect of substituted position to ring systems by alkoxymethylene groups. In compounds Nos. 3, 7 and 8, alkoxymethylene groups were attached to the cyclohexane ring, and others were attached to the benzene ring by alkoxymethylene groups. If the comparison between cyclohexane series (Nos. 3, 7 and 8) and benzene series (No. 2), the clearing points of cyclohexane series are higher than that of benzene series. We assumed that large flexibility of alkoxymethylene groups caused low clearing points of alkoxymethylene-substituted mesogens.[3] But, in above cyclohexane series, it can be considered that the lowering effect to the clearing points based on flexibility of alkoxymethylene groups is reduced by the bulk of cyclohexane ring. This is the reason why cyclohexane series exhibit higher clearing points than benzene series.

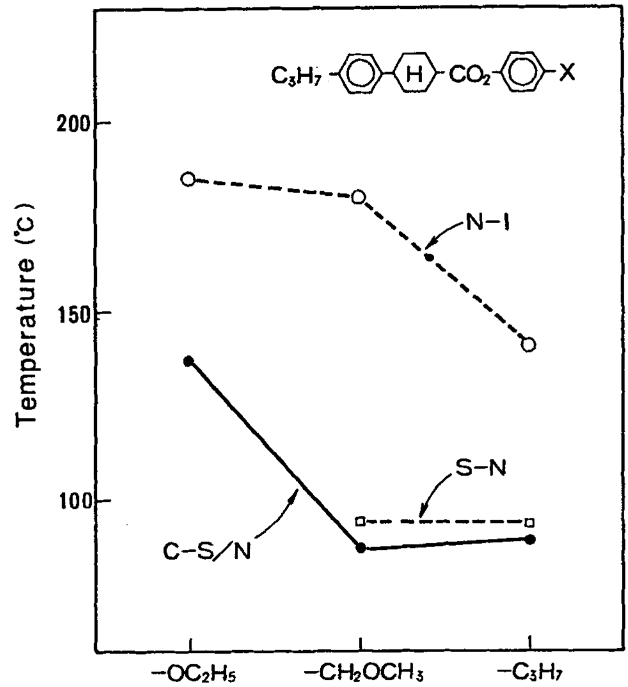


FIGURE 4 Transition temperatures versus substituted groups X, which are ethoxy-, methoxymethyl- and propyl-.

The examples shown in Figures 2 to 5 illustrate the magnitude of the effect of terminal groups on the transition temperatures. The transition temperatures of alkoxymethylene series (III) are compared with appropriate alkoxy- or alkyl-substituted series.[6,7] In each figure, it is noticed that the melting points and clearing points of alkoxymethylene series are lower than those of alkoxy series. But, on comparison alkoxymethylene series and alkyl series, the relationships between terminal groups and transition temperatures are variable. For instance, in Figure 4, clearing points of alkoxymethylene series is higher than that of alkyl series. In Figures 4 and 5, on the contrary, clearing points of alkoxymethylene series are lower than those of alkyl series.

From above results, it is concluded that alkoxymethylene groups have effect on decreasing the transition temperatures compared with alkoxy groups. This result agrees with that previously reported on two ring systems (I) and (II). On the comparison alkoxymethylene

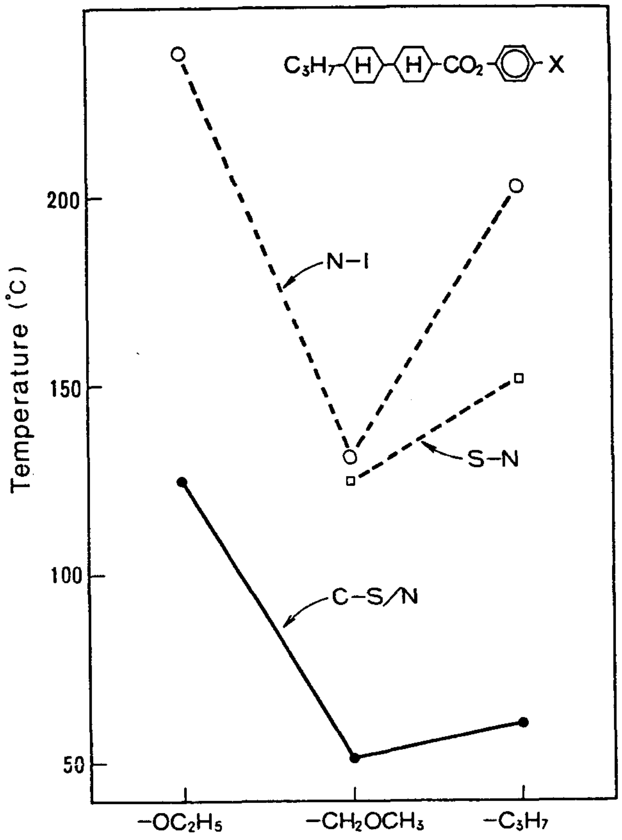


FIGURE 5 Transition temperatures versus substituted groups X, which are ethoxy-, methoxymethyl- and propyl-.

groups with alkyl groups, however, we could not arrange in order of decreasing transition temperatures. This is the subject for future study.

Acknowledgments

The authors would like to thank M. Yoshida, H. Ohkawa and Y. Okabe who carried out the experimental chemical work and the performance of the physical measurement.

References

1. T. Kitamura, A. Mukoh and T. Fujii, *Mol. Cryst. Liq. Cryst.*, **108**, 333 (1984).
2. T. Kitamura, A. Mukoh, S. Era and T. Fujii, *Mol. Cryst. Liq. Cryst.*, **112**, 319 (1984).

3. T. Kitamura, A. Mukoh, S. Era and T. Fujii, *Mol. Cryst. Liq. Cryst.*, **130**, 231 (1985).
4. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, presentation at the 8th International Liquid Crystal Conference, Kyoto (1980).
5. H. J. Deutscher, B. Laaser, W. Dolling and H. Schubert, *J. Prakt. Chem.*, **320**, 191 (1978).
6. R. Steinstrasser and F. Del Pino, US-Pat. 4 136 053 (1979).
7. R. Eidenschink, J. Krause, L. Pohl and J. Eichler, *Liq. Cryst. Proc. Int. Conf.*, (edited by S. Chandrasekhar), Heydon, London (1980).