This article was downloaded by: [Tomsk State University of Control Systems and Radio]

On: 19 February 2013, At: 13:35

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered

office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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 <sup>a</sup> , Akio Mukoh <sup>a</sup> , Tsunenori Fujii <sup>b</sup> & Kenji Suzuki <sup>b</sup> <sup>a</sup> Hitachi Research Laboratory, Hitachi Ltd., 4026 Kuji, Hitachi, Ibaraki, Japan, 319-12

<sup>b</sup> Central Research Laboratory, Kanto Chemical Co., Inc., 2048 Inari, Soka, Saitama, Japan, 340

Version of record first published: 28 Mar 2007.

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: <a href="http://dx.doi.org/10.1080/00268948708082978">http://dx.doi.org/10.1080/00268948708082978</a>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1987, Vol. 149, pp. 177-184 Photocopying permitted by license only © 1987 Gordon and Breach Science Publishers S.A. 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 threering 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, <sup>1,2,3</sup> we reported the nematic properties of new mesogens with alkoxymethylene groups as terminal groups. These compounds were 4-alkoxymethylene-substituted-phenyl 4'-alkylcylohexanes (I)<sup>1</sup> and 4-alkoxymethylene-substituted-phenyl 4'-alkylcyclohexanecarboxylates (II).<sup>2,3</sup> 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 threering systems (III) are synthesized and their mesomorphic properties are examined compared with the corresponding alkoxy- or alkylsubstituted esters.

$$R - H - CO_2 - CH_2 \cdot n^0 R'$$
 (I)  
 $R - H - CO_2 - CH_2 \cdot n^0 R'$  (II)  
 $C_3 H_7 - X - Y - CO_2 - CH_2 \cdot CH_3$  (III)  
 $R \cdot R' = alkyl , n = 1 to 5$   
 $X \cdot Y = benzene, cyclohexane$ 

The compounds (III) are prepared as shown in Figure 1. The methoxymethyl-substituted-phenol is synthesized by a previously reported<sup>3</sup> 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  $\boldsymbol{X}$  and  $\boldsymbol{Y}$  are benzene or cyclohexane.

TABLE I

Single cor solid phat	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—	ade. The abbrevir he absence of pha	itions mean res	pectively, C; indicated by
NO.	Structure	Transition Ter	Transition Temp.(°C) C-S/N S-N N-	(°C)
-	с₃н, ⟨○⟩-⟨○⟩-со₂-⟨○⟩-сн₂осн₃	103	106	191
2	C3H, (H) (O) -CO2 (O) -CH2OCH3	62	I	131
က	CH₃OCH₂ ⟨H⟩-⟨O⟩-Co₃ ⟨Ô⟩-C₃H,	95	105	164
4	С3Н,-(()-(Н)-СО2 -(()-СН2ОСН3	87	94	180
ഹ	С,4,-(Н)-(Н)-с0,-(О)-сн,осн,	51	125	131
9	C3H,-{H}-{H}-CO2-{	24	130	168
7	С³Н, ⟨Н⟩-⟨О}-СО, -⟨Н}-СН2ОСН3	92	1	185
œ	сн₃осн₂ ⟨Н⟩-Со₂-⟨Н⟩-С₃н,	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)<sup>1</sup> and (II),<sup>2,3</sup> tendency to form enantiotropic mesophases of alkoxymethylene series is lower than alkoxy series.<sup>4,5</sup> 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.

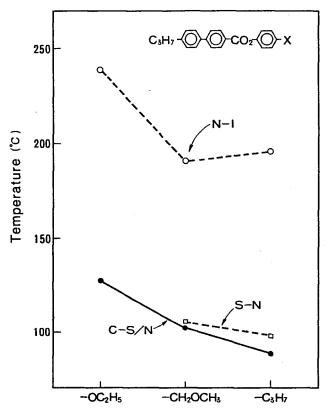


FIGURE 2 Transition temperatures versus substituted groups X, which are ethoxymethoxymethyl- and propyl-.

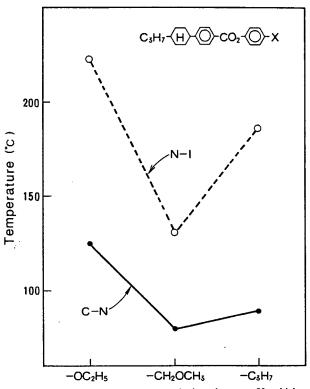


FIGURE 3 Transition temperatures versus substituted groups X, which are ethoxymethoxymethyl- and propyl-.

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.<sup>3</sup> 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.

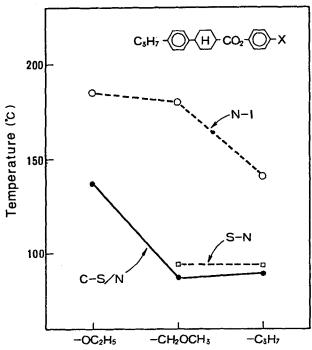


FIGURE 4 Transition temperatures versus substituted groups X, which are ethoxymethoxymethyl- and propyl-.

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.<sup>6,7</sup> 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

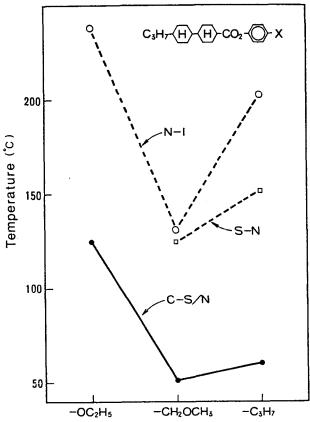


FIGURE 5 Transition temperatures versus substituted groups X, which are ethoxymethoxymethyl- and propyl-.

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).
- 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).