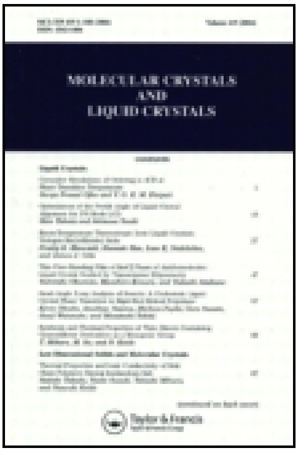

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Phase Structure and Polymorphism of n-Alkyl Monoesters of Biphenyl-4,4′-dicarboxylic Acid

J. Swadesh [a] & H. Fischer [a]

[a] Alpha-Beta Technology, Innovation drive, Worcester, MA, 01006, U.S.A.

[b] Centre for Polymer Research, Faculty of Chemical Technology, University of Technology, Eindhoven, P.O. Box 513, Eindhoven, 5600, MB, The Netherlands

Version of record first published: 24 Sep 2006.

To cite this article: J. Swadesh & H. Fischer (1996): Phase Structure and Polymorphism of n-Alkyl Monoesters of Biphenyl-4,4′-dicarboxylic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 275:1, 175-181

To link to this article: http://dx.doi.org/10.1080/10587259608034072

*Mol. Cryst. Liq. Cryst.*, 1996, Vol. 275, pp. 175–181
Reprints available directly from the publisher
Photocopying permitted by license only

# Phase Structure and Polymorphism of *n*-Alkyl Monoesters of Biphenyl-4,4′-dicarboxylic Acid

J. SWADESH

*Alpha-Beta Technology, Innovation drive, Worcester, MA 01006, U.S.A.*

H. FISCHER*

*Centre for Polymer Research, Faculty of Chemical Technology, University of Technology, Eindhoven, P.O. Box 513, Eindhoven, 5600 MB, The Netherlands*

*(Received June 20, 1995; in final form August 9, 1995)*

The phase structure of the *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid has been investigated using optical microscopy and X-ray diffraction techniques. A polymorphism N, $S_C$, $S_F$ and crystal B has been found which is understandable because of the essentially 2-d correlated smectic F phase with only a small interlayer correlation and the extensive 3-d correlation of the smectic B phase. The formation of dimers via H-bridges and an intercalation of the dimers which is active within the first 4 to 5 $CH_2$ groups of the tail groups of the dimers in both ends have been proven by X-ray diffraction.

*Keywords: Liquid crystals, smectic phases, textures, X-ray diffraction*

## 1. INTRODUCTION

One of the first substances, where liquid crystalline properties were recognised was 4′-methyl-biphenyl-4-carboxylic acid.[1] This substance transforms from a crystalline phase to a nematic phase at 258°C before transforming into an isotropic liquid at 292°C. More systematical investigations of a homologous series of this substance and of 4′-*n*-alkoxy-biphenyl-4-carboxylic acids show the appearance of a smectic C phase with increasing lengths of the *n*-alkoxy tail group.[2] It was recognised that in both cases a dimerisation of two molecules via H-bonds was the reason for the display of liquid crystalline properties. The dimerisation of carboxylic acids is very pronounced and the stability of the dimers is quite high. Dimerisation is also present in the case of soaps and acetic acid has only been found in dimers even in the gas phase. Preliminary investigations of the *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid have shown that all derivatives from the monoethylester to the mono *n*-pentadienylester exhibit liquid crystalline behaviour.[3–4] In addition to a nematic phase, most of the compounds display three different smectic phases. It was assumed that the polymorphism displayed in N, $S_C$, $S_B$ and $S_E$.[3,4] However, this was only concluded from optical investigations.

---

* To whom all correspondence should be sent.

The purpose of this work is a structural characterisation of the smectic phases found and of the polymorphy of the system of mono-*n*-alkylesters of biphenyl-4,4′-dicarboxylic acid.

## 2. RESULTS AND DISCUSSION

Structural investigations have been carried out using substances with the general chemical formula shown in Figure 1. The phase behaviour of these substances has been described previously.[3,4] The authors have found the existence of three smectic phases for $n = 3$–$14$ and a nematic phase for $n = 4$–$8$ and $11$–$15$. The structure of the smectic phases remains stable with respect to a change of the length of the tail group. This could be proved by mixing experiments of the substances with $n = 7$ and $n = 11$ and polarisation optical microscopy investigations. The detailed structure of the smectic phases was of main interest. Therefore, X-ray diffraction experiments and optical

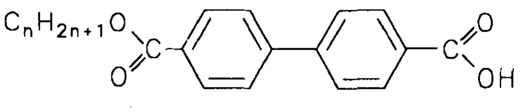

FIGURE 1 Chemical structure of the investigated substances.

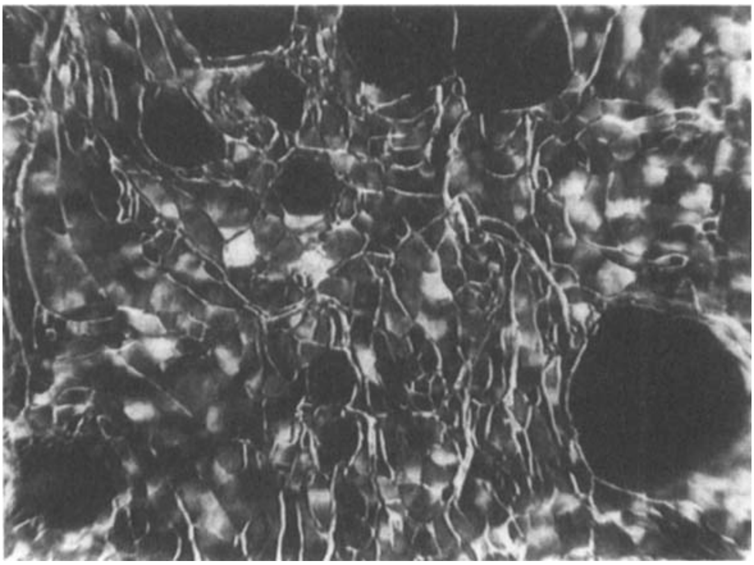

FIGURE 2 POM micrograph of the substance with $n = 11$, 90°C, crossed polarisers, smectic B phase, *mosaic* texture. See Color Plate III.

investigations have been carried out using several techniques. Typical textures for the different phases were found by optical investigations. The low temperature smectic phase has been identified to be a crystal B type (see Fig. 2). The texture of this phase is a very distinguished *mosaic* texture, a texture displayed by B, E or G phases.[5] X-ray investigations on oriented samples confirm a crystal B-like structure. Here the structure is more solid than in the true smectic phases.[6] In Figure 3 very pronounced layer reflections (001 and 002) are visible and perpendicular to them one sharp reflection indicating a well-ordered layered structure of the crystal B type. The first and the high temperature smectic phase shows in contrast to Ref. 3 clear visible *schlieren* textures (see Fig. 4). The difference in the observed textures may arise due to the fact that in both studies a different method of sample preparation was used. The casting from a solvent could cause the formation of metastable phases.

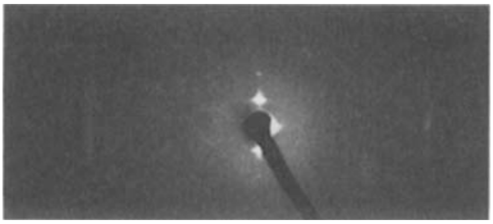

FIGURE 3 X-ray diffraction pattern of the substance with $n = 11$ at 90°C, magnetic field oriented, arrow indicates field direction.

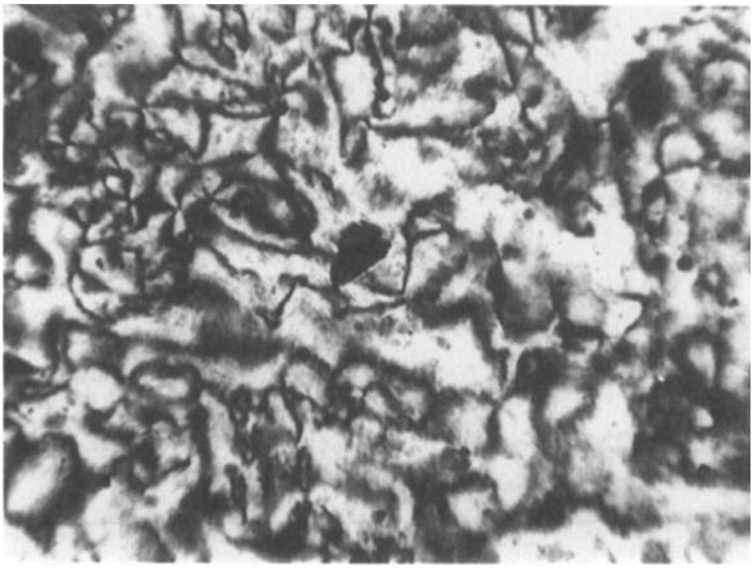

FIGURE 4 POM micrograph of the substnace with $n = 11$, 150°C, crossed polarisers, smectic F phase, *schlieren* texture. See Color Plate IV.

*Schlieren* textures are observed for smectic A, C and F phases.[5,7] However, miscibility studies supported by X-ray investigations have identified the second smectic phase as smectic F and the high temperature phase as smectic C, consistent with Ref. 3. Clear differences between both phases are observable in a Goniometer plot of the substance with $n = 11$ at temperatures of 210°C and 150°C (see Fig. 5). While the smectic C phase shows only one diffuse reflection in the wide angle area, the smectic F phase is characterised by one sharp and two diffuse reflections.[6,8-11] Finally, Figure 6 shows the texture typical for the transition from smectic C to nematic.[5] The phase structure diagram of the substances is now displayed in Figure 7.

A possible polymorphism CFB has already been proposed by Saeva since the proposed sequence of liquid crystalline states has been specified as $S_G/S_E$, $S_B$, $S_F$, $S_C$, $S_A$, N/Ch. However, the smectic B and smectic F phase are not being reported in the same sequence but on the basis of the level of structural order of layers, the smectic F phase would be expected to be a higher temperature modification relative to the smectic B phase.[12] The smectic F phase is in fact characterised as an essentially 2-d phase with only a small interlayer correlation[6,8-11] whereas the B phase has been found either with incomplete 3-d correlation or with extensive 3-d correlation.[8,13,14] A similar classification has been made by Goodby and Gray;[15] a distinction between the hexatic B and the crystal B (smectic L) phase has been made. The smectic F phase is, however, described as a truly hexatic phase. Therefore, a polymorphism as found is not unusual.

Small angle X-ray investigations of the substance with $n = 11$ show a steady increase from 39.5 Å (high temperature smectic phase) to 42 Å (low temperature smectic phase)

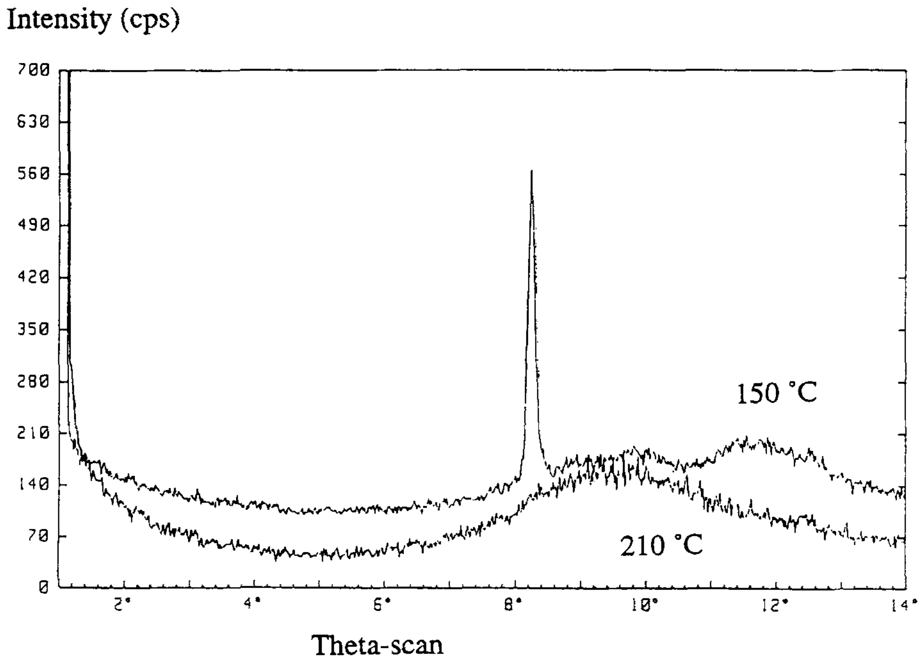

FIGURE 5 Diffractogram of $n = 11$ at 150°C (smectic F phase) and at 210°C (smectic C phase).

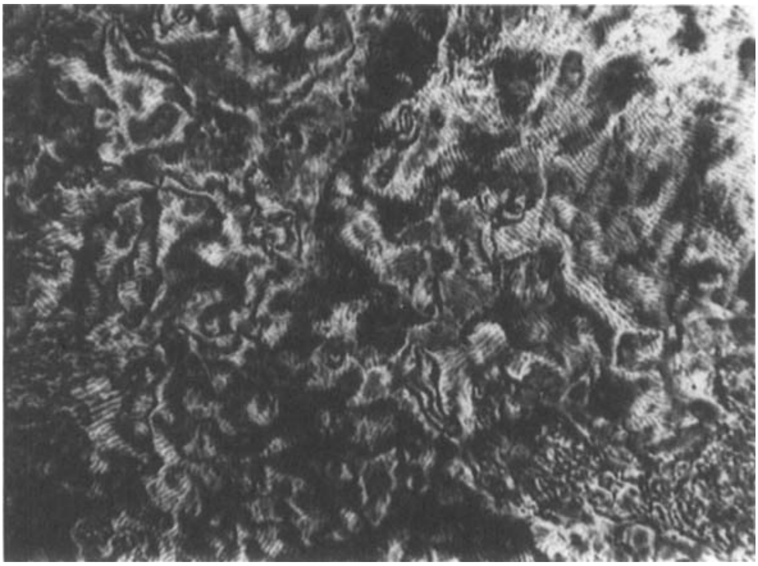

FIGURE 6 POM micrograph of the substance with $n = 11$, 220°C, crossed polarisers, transition smectic C to nematic. See Color Plate V.

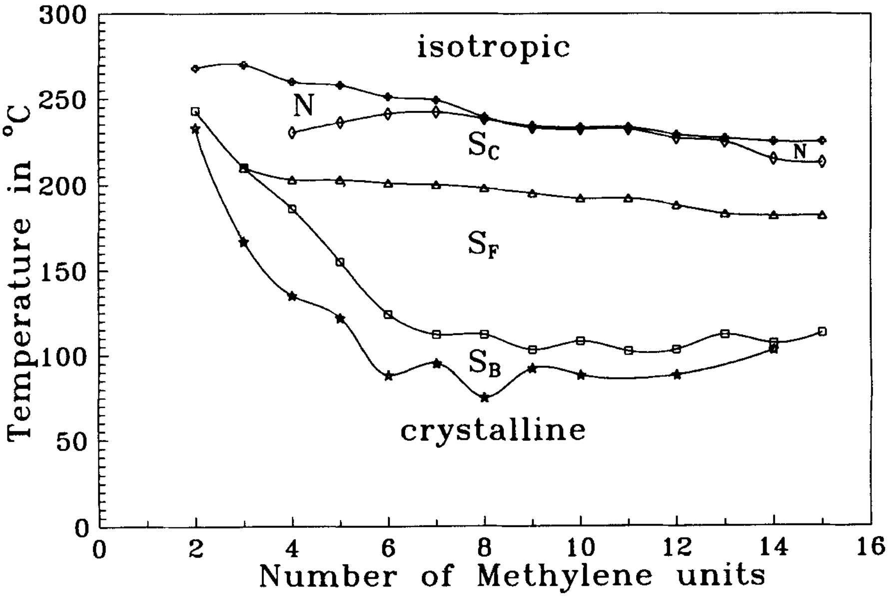

FIGURE 7 Phase structure diagram of the investigated substances.

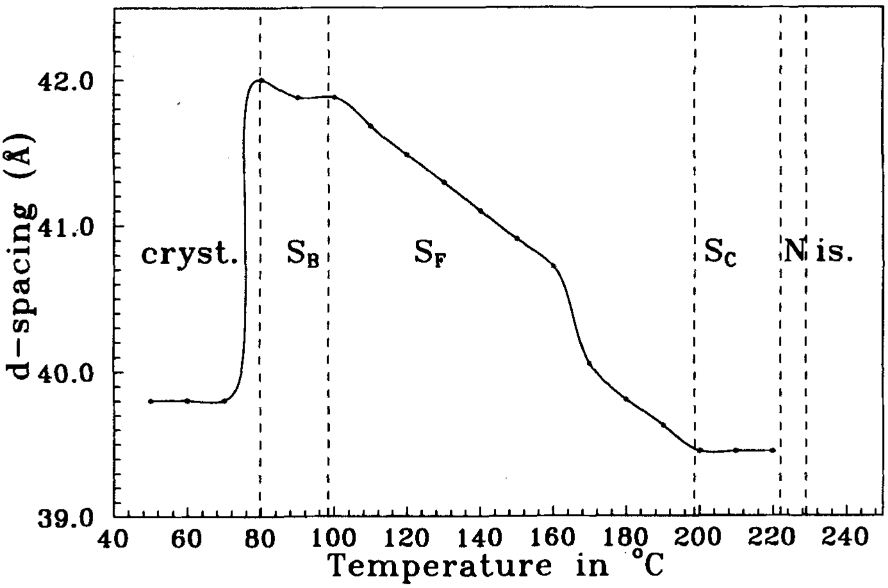

FIGURE 8 Layer spacing as a function of temperature for the substance with $n = 11$.

in layer thickness with a decrease in temperature (see Fig. 8). This also suggests the existence of tilted high temperature smectic phases like smectic C and smectic F above a nontilted low temperature crystal B phase. The smectic F phase, existing over a remarkable wide temperature range, seems to play an active transition from a nonordered fluid-like layered structure to a very well ordered solid-like layered structure as the steady increase in layer thickness suggests. At no time during the heating cycle does the layer thickness fall to the extended length of a single molecule, nor rise to the length of two extended molecules. The length of a single molecule is only about 26 Å so that an intercalated packing in the smectic structure of H-bridged dimers (see Fig. 9) is very likely. The interaction should be active within the first 4 to 5 $CH_2$ groups of the tail groups of the dimers in both ends.

## 3. EXPERIMENTAL

Liquid crystalline behaviour was determined visually with a hot stage mounted on a Zeiss optical microsocpe. Structural characterisation was performed using Cu-$K_\alpha$

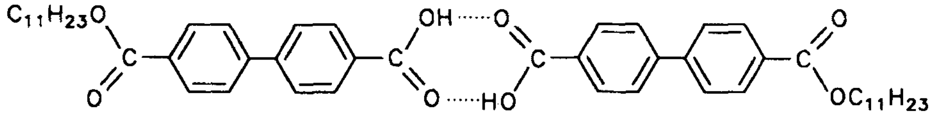

FIGURE 9 Chemical structure of the H-bonded dimer.

radiation monochromized by a graphite crystal monochromator and a flat film camera or a Guinier film camera and a Guinier Goniometer from HUBER. The cameras were equipped with hot stages, the temperature accuracy was ± 0.5 K. Oriented samples, sealed in Lindemann capillaries, were obtained using the support of a magnetic field of approximately 1 T by cooling down from 10 K above the clearing point into the mesophase with a rate of 1 K/hr.

## Acknowledgement

The authors would like to thank Mrs. A. Mädike for support during the optical investigations.

## References

1. F. Reinitzer, *Monatshefte f. Chemie*, **9**, 421 (1888).
2. G. W. Gray, J. B. Hartley and B. Jones, *J. Chem. Soc.*, 1412 (1955).
3. S. D. Cohen, C. A. R. Diuguid, J. C. Poirier and J. K. Swadesh, *Mol. Cryst. Liq. Cryst.*, **78**, 135 (1981).
4. J. K. Swadesh and J. C. Poirier, *Mol. Cryst. Liq. Cryst.*, **92**, 119 (1983).
5. D. Demus and L. Richter, in *Textures in Liquid Crystals*, Verlag Chemie Weinheim, New York, 136, 177, 192 (1978).
6. G. S. Attard, R. W. Date, C. T. Imrie, G. R. Luckhurst, S. J. Roskilly, J. M. Seddon and L. Taylor, *Liq. Cryst.*, **16**, 529 (1994).
7. E. Gorecka, W. Pyzuk, A. Krowcynski and J. Przedmojski, *Liq. Cryst.*, **14**, 1537 (1993).
8. P. A. C. Ganes, A. J. Leadbetter and Z. G. Wrighton, *Mol. Cryst. Liq. Cryst.*, **66**, 247 (1981).
9. S. Gierlotka, J. Przedmojski and B. Pura, *Liq. Cryst.*, **3**, 1837 (1988).
10. V. G. K. M. Pisipati, N. V. S. Rao, B. Chidambara Sastry, P. Bhaskara Rao, G. P. Rani and P. R. Alapati, *Liq. Cryst.*, **9**, 565 (1991).
11. S. Diele, D. Demus and H. Sackmann, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 217 (1980).
12. F. D. Saesa, in *Liquid Crystals – The Fourth state of Matter*, Marcel Dekker Inc., New York and Basel, 195 (1979).
13. D. E. Moncton and R. Pindak, *Phys. Rev. Lett.*, **43**, 701 (1979).
14. P. S. Pershan, G. Aeppeli, J. D. Lister and R. J. Birgenau, *Mol. Cryst. Liq. Cryst.*, **67**, 205 (1981).
15. G. W. Gray and J. W. C. Goodby, in *Smectic Phases – Textures and Structures*, Leonhard Hill, Glasgow and London, 1984.