Molecular Crystals and Liquid Crystals

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

The Classification of the Liquid Crystalline Modificatons in some Homologous Series

A. Biering [a b] , D. Demus [a b] , G. W. Gray [a b] & H. Sackmann [a b]

[a] Sektion Chemie, Martin-Luther Universität Halle, 402 Halle(S), Mühlpforte, 1, GDR

[b] Department of Chemistry, The University Hull, Hull HU 6 7 RX, England

Version of record first published: 21 Mar 2007.

To cite this article: A. Biering , D. Demus , G. W. Gray & H. Sackmann (1974): The Classification of the Liquid Crystalline Modificatons in some Homologous Series, Molecular Crystals and Liquid Crystals, 28:3-4, 275-292

To link to this article: http://dx.doi.org/10.1080/15421407408082825

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 275-292

Printed in Dordrecht, Holland

The Classification of the Liquid Crystalline Modifications in some Homologous Series[†]

A. BIERING, D. DEMUS, G.W. GRAY and H. SACKMANN

Sektion Chemie, Martin-Luther Universität Halle,
402 Halle(S), Mühlpforte 1 GDR
Department of Chemistry,
The University Hull, Hull HU 6 7 RX, England

(*Received December 12, 1973*)

SUMMARY

By means of miscibility investigations, the types of liquid crystalline modifications in the following homologous series have been established: trans-4-*n*-alkoxycinnamic acids (I); *trans*-4-*n*-alkoxy-3-chlorocinnamic acids (II); 6-*n*-alkoxy-2-naphthoic acids (III); 6-*n*-alkoxy-5-halogeno-2-naphthoic acids, halogen = chloro (IV), bromo (V), iodo (VI); 4′-*n*-alkoxy-3′ bromobiphenyl-4-carboxylic acids (VII); 4-[4-*n*-alkoxybenzylideneamino]biphenyls (VIII); 2-[4-*n*-alkoxybenzylideneamino]-fluorenes (IX) and -fluorenones (X); 2,7-di-[4-*n*-alkoxybenzylideneamino fluorenones (XI); *n*-alkyl 4-[4-phenylbenzylideneamino cinnamates (XII).

In the series I-VII and XI, besides nematic phases, the smectic type C (variants of polymorphism N; SC, N; SC) occurs. In series IX-X, besides nematic phases, the smectic type A (variants of polymorphism N; SA, N; SA) occurs. In Series VIII the variants of polymorphism N; SB, SA, N; SA exist.

In series XII the new variant of polymorphism SE, SB, SA has been found besides the variant SB, SA, N. The variant SE, SB, SA has also been observed in the compound 4-[4-*n*-nonyloxybenzylideneamino]-4′-chlorobiphenyl.

Some remarks are made on smectic polymorphism and on the structure of the smectic modification of the type E.

INTRODUCTION

This paper continues the communications concerning the classification of liquid crystalline modifications by means of miscibility investigations.[1] These investiga-

---

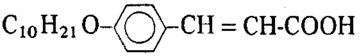
[†] Paper No. 20 in the series "Relations of isomorphism between liquid crystalline phases"

tions are especially effective, if the polymorphism in a homologous series is known. A knowledge of the trend of the transition temperatures within a homologous series often allows one to classify all liquid crystalline modifications of the series if several members of the series, or sometimes only one, are examined by miscibility studies discussed later. The numbers between two symbols are line modifications which occur in some homologous series[3-10] are defined in such a way.

MATERIALS

In the following sub-sections the substances investigated are listed. The transition scheme gives the types of liquid crystalline modifications from left to right in the sequence of their appearance with increasing temperature. The symbols used are: C = crystalline solid state; N, SA, SC, SB, SE = liquid crystalline states of the types nematic, smectic A, C, B, E[2] respectively; I = isotropic liquid state. The characterization of the modifications with these symbols is the result of the miscibility investigations in Section 3. The numbers between two symbols are the temperatures (in degrees Celsius) of the transition between the two modifications. Some remarks about observations relating to textures are given. In this work we have used the substances originally described in References 3-15; small differences in the transition temperatures may arise from the use of thermometer corrections and other experimental differences.

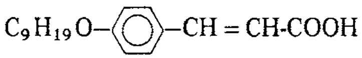
No 1† *trans*-4-*n*-decyloxycinnamic acid[3]



C 135.5 SC 143 N 166 I

Substances No 1-13 show schlieren textures [16],[17], [18] in the smectic C state.

No 2 *trans*-4-*n*-nonyloxy-3-chlorocinnamic acid[4]



C 124 SC 128.2 N 136 I

No 3 *trans*-4-*n*-octadecyloxy-3-chlorocinnamic acid[4]

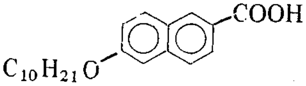
C 118 SC 120.5 I

---

† Transitions are:

$$\text{Crystal} \xrightarrow{135.5^\circ} \underset{\text{Phase}}{\text{Smectic C}} \xrightarrow{143^\circ} \underset{\text{Phase}}{\text{Nematic}} \xrightarrow{166^\circ} \underset{\text{Phase}}{\text{Isotropic}}$$

No 4 6-*n*-decyloxy-2-naphthoic acid[5]

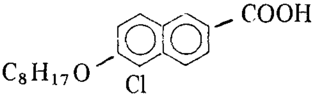


C 139.8 SC 147.1 N 179.8 I

No 5 6-*n*-hexadecyloxy-2-naphthoic acid[5]

C 107.5 SC 157.5 I

No 6 6-*n*-octyloxy-5-chloro-2-naphthoic acid[6]



C 167.6 SC 181.3 N 197 I

No 7 6-*n*-hexadecyloxy-5-chloro-2-naphthoic acid[6]

C 141 SC 176 I

No 8 6-*n*-nonyloxy-5-bromo-2-naphthoic acid[6]

C 166.5 SC 176 N 189.8 I

No 9 6-*n*-hexadecyloxy-5-bromo-2-naphthoic acid[6]

C 137.5 SC 169.5 I

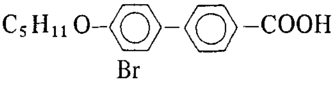
No 10 6-*n*-dodecyloxy-5-iodo-2-naphthoic acid[6]

C 147 SC 167.5 N 171.2 I

No 11 6-*n*-octadecyloxy-5-iodo-2-naphthoic acid[6]

C 126 SC 161.5 I

No 12 4′-*n*-pentyloxy-3′-bromobiphenyl-4-carboxylic acid[7]

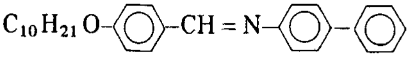


C 191 SC 193 N 233 I

No 13 4′-*n*-octadecyloxy-3′-bromobiphenyl-4-carboxylic acid[7]

C 119.5 SC 193.5 I

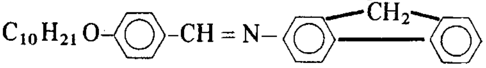
No 14 4-[4-*n*-decyloxybenzylideneamino]biphenyl[8]



C 122 SB 139.8 SA 156.5 N 157.5 I

Smectic A appears in a focal conic texture[16, 17, 18] and smectic B also shows a focal conic texture but with a diminished number of discontinuities[16, 17, 19].

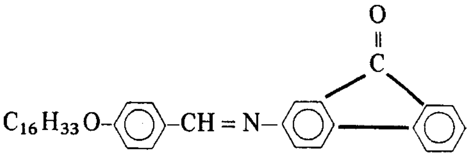
No 15 2-[4-*n*-decyloxybenzylideneamino]flurorene[8]



C.113.5 SA 167 N 175.5 I

Smectic A shows a focal conic texture or a homeotropic texture[16, 17, 18].

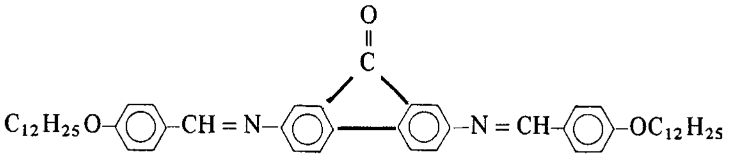
No 16 2-[4-*n*-hexadecyloxybenzylideneamino]fluorenone[8]



C 91.5 SA 115 N 126 I

Smectic A shows a focal conic texture or a homeotropic texture[16, 17, 18].

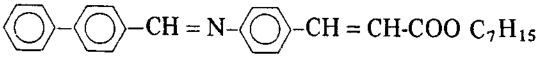
No 17 2,7-di-[4-*n*-dodecyloxybenzylideneamino]fluorenone[8]



C 130 SC 261 N 266 I

Smectic C appears in a schlieren texture or in the broken focal conic texture[16, 17, 18].

No 18 *n*-heptyl–4-[4'-phenylbenzylideneamino]cinnamate[9]



C 81.9 SE 94.4 SB 160.8 SA 198 I

Smectic A: focal conic texture[16, 17, 18]; smectic B: focal conic texture with a diminished number of discontinuities[16, 17, 19]; smectic E focal conic texture with transverse stripes or concentric arcs[2, 15]. Smectic E may also appear in a mosaic texture with grey interference colours[19].

During the transition smectic A to smectic B transient transverse stripes (transition bars[22]) are visible.

No 19 *n*-decyl–4-[4′-phenylbenzylidenneamino]cinnamate[9]

C 72.5 SE 89.9 SB 154 SA 188.8 I
The textures correspond to those of No 18

No 20 4-[4-*n*-nonyloxybenzylideneamino]-4′-chlorobiphenyl

C 103 SE 146.5 SB 206 SA 251.5 I
The textures correspond to those of No 18

The liquid crystalline properties of the following substances Numbers 21-24 have been described already in former publications. They have been applied as reference substances for the miscibility investigations.

No 21 4-*n*-dodecyloxybenzoic acid[11, 12]

(SC, N)

No 22 di-*n*-nonyl–4,4′-azoxycinnamate[13]

(SC, SA)

No 23 4-[4-*n*-nonyloxybenzylideneamino]azobenzene[14]

(SB, SA, N)

No 24 diethyl *p*-terphenyl-4,4″-dicarboxylate[15]

(SE, SA)

DIAGRAMS OF STATES

The diagrams of state (temperature-concentration diagrams) for the following 21 systems were obtained by means of microscopical observations, in polarized light, of samples mounted between a glass slide and a coverslip on a heating stage.

Since a simple type of diagram occurs in most cases, the contact method has been applied. This method yields the type of the diagram, the right transition temperatures for three-phase transitions, and maxima and minima in the transition curves, but not the concentrations corresponding to these temperatures. In these cases the concentration axes are not graduated.

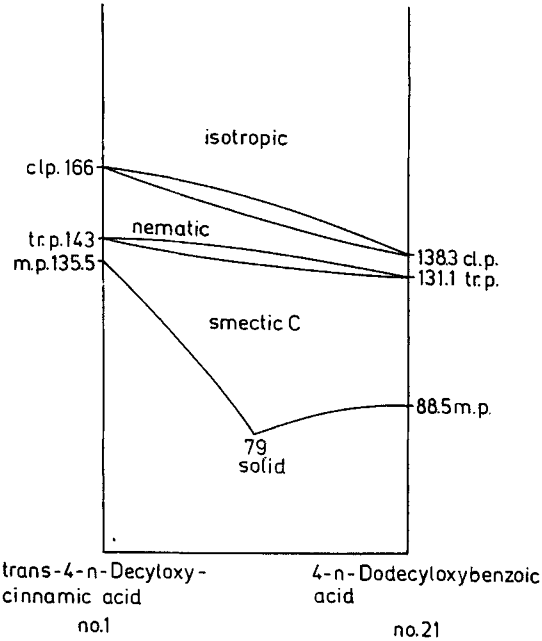


FIGURE 1. System 1

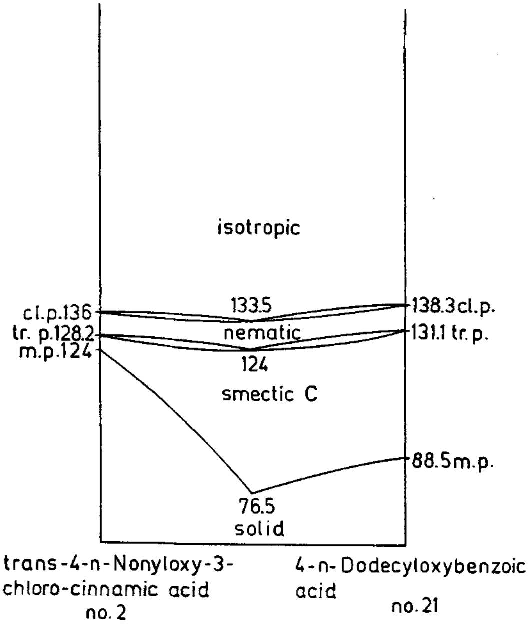


FIGURE 2. System 2

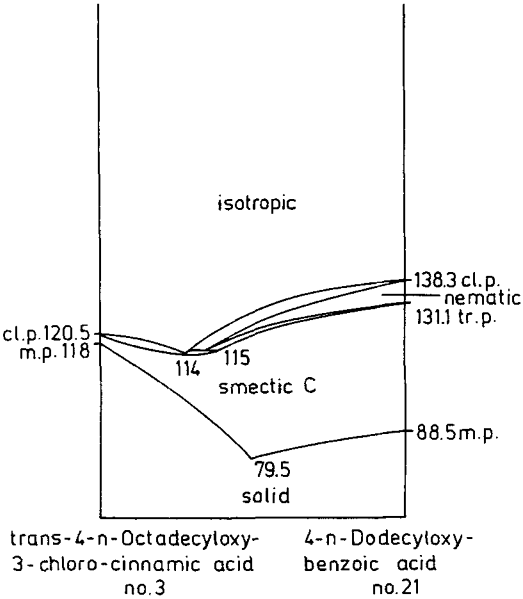


FIGURE 3. System 3

In some cases, especially if a more complicated diagram exists, the transitions of mixtures with given concentrations have been investigated (concentration in mole percent).

The following abbrevations have been used: m.p. = melting point, tr.p. = transition point, cl.p. = clearing point; the temperatures corresponding to maxima and minima in the transition curves and to three-phase transitions are given in the Figures 1-3.

System 1: Figure 1
„ 2: Figure 2
„ 3: Figure 3

System 4

6-*n*-Decyloxy-2-naphthoic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 1; minimum in the melting curve is at 78°C.

System 5: Figure 4

System 6

6-*n*-Octyloxy-5-chloro-2-naphthoic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 1; minimum in the melting curve is at 79°C.

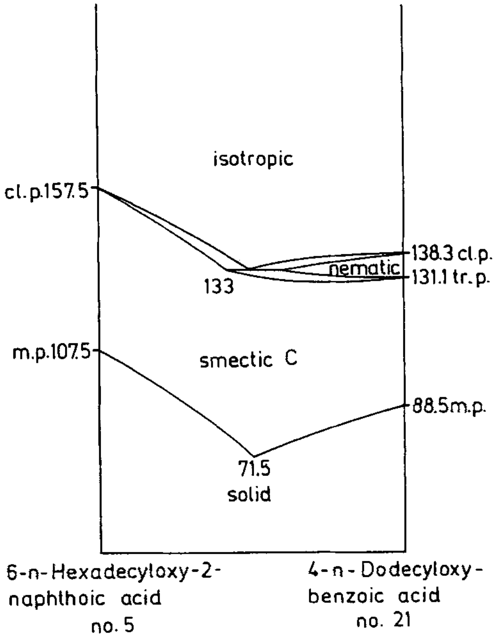


FIGURE 4. System 5

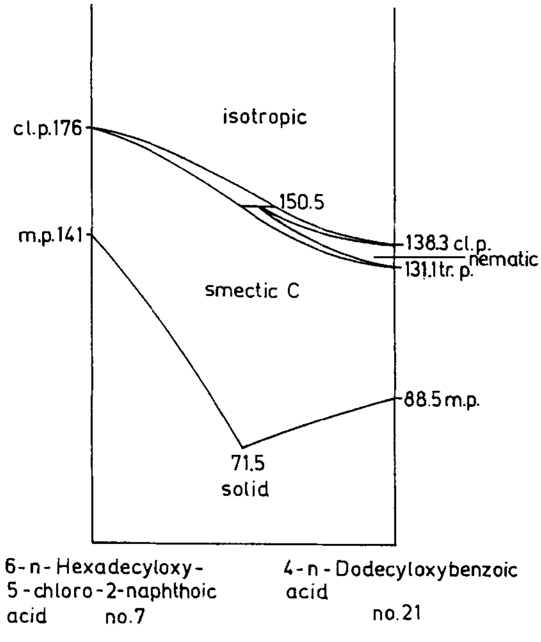


FIGURE 5. System 7

System 7: Figure 5

System 8
6-*n*-Nonyloxy-5-bromo-2-naphthoic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 1; minimum in the melting curve is at 71.2°C.

System 9
6-*n*-Hexadecyloxy-5-bromo-2-naphthoic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 5; three–phase transition, smectic C+ isotropic liquid → *nematic at* 153°C; *minimum in the melting curve is at* 75.5°C.

System 10
6-*n*-Dodecyloxy-5-iodo-2-naphthoic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 1; minimum in the melting curve is at 83°C.

System 11
6-*n*-Octadecyloxy-5-iodo-2-naphthoic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 5; three-phase transition, smectic C + isotropic liquid → nematic at 148°C; minimum in the melting curve is at 84°C.

System 12
4′-*n*-Pentyloxy-3′-bromobiphenyl-4-carboxylic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 1; minimum in the melting curve is at 67.5°C.

System 13
4′-*n*-Octadecyloxy-3′-bromobiphenyl-4-carboxylic acid/4-*n*-dodecyloxybenzoic acid. The diagram of state corresponds to Fig. 5; three-phase transition, smectic C + isotropic liquid → nematic at 153.5°C; minimum in the melting curve is at 68.5°C.

System 14: Figure 6
System 15: Figure 7
System 16: Figure 8

System 17
4′-*n*-Pentyloxy-3′-bromobiphenyl-4-carboxylic acid/2,7-di-[4-n-dodecyloxybenzylideneamino] fluorenone. The diagram of state corresponds to Fig. 2. Minima in the curves of the transitions, isotropic liquid → nematic at 223°C, nematic → smectic C at 186°C, smectic C → solid at 119°C.

System 18: Figure 9

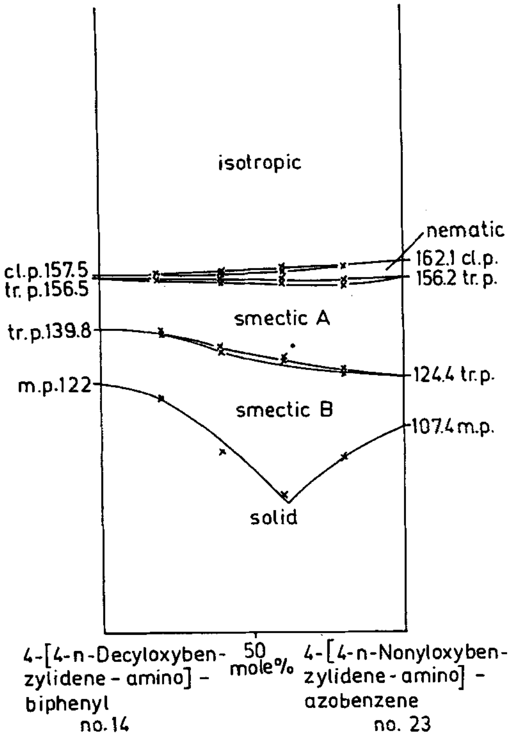


FIGURE 6. System 14

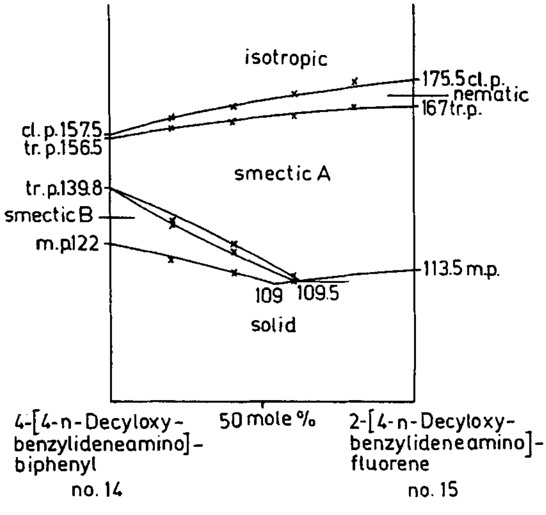


FIGURE 7. System 15

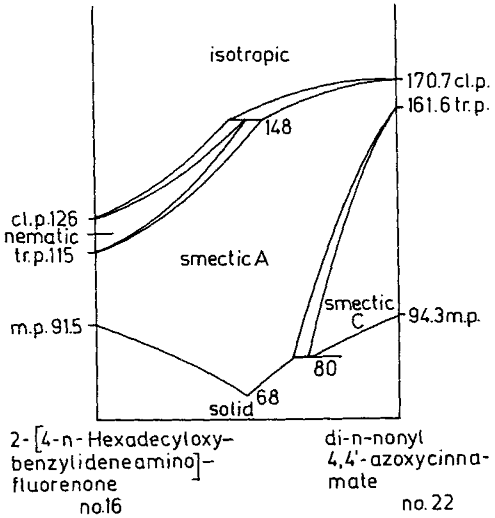


FIGURE 8. System 16

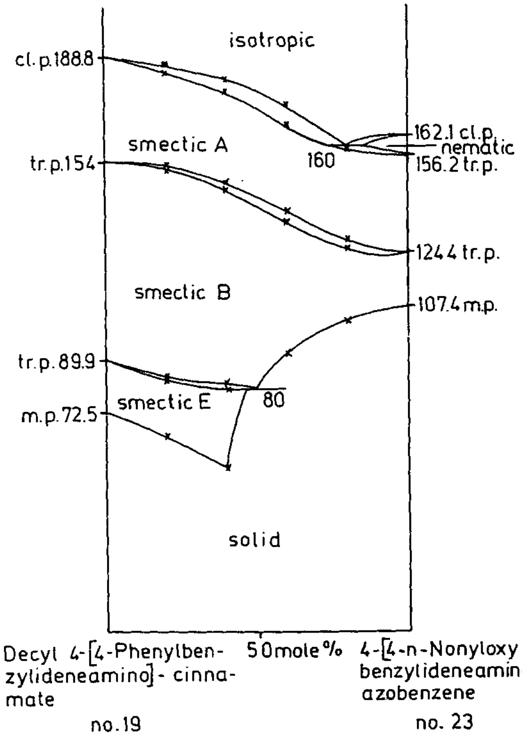


FIGURE 9. System 18

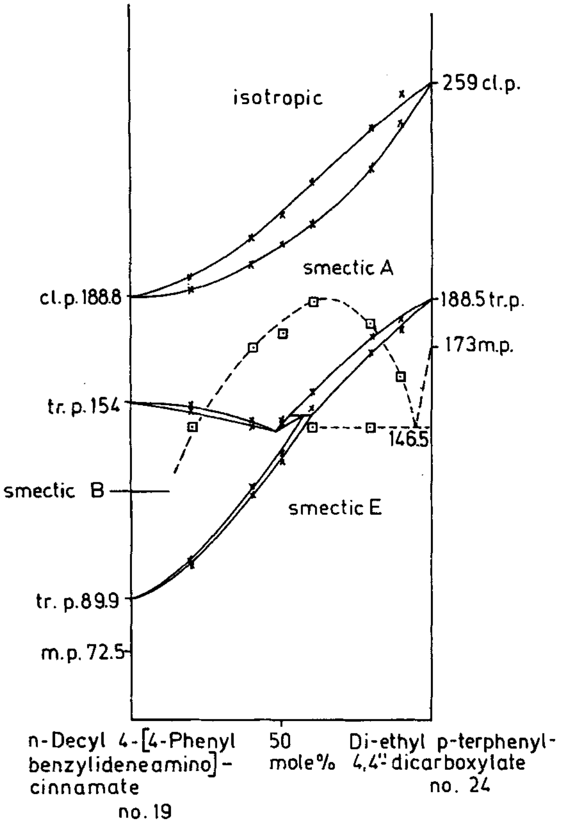


FIGURE 10. System 19

System 19: Figure 10
The melting curve (points are drawn as squares) shows a maximum. For this reason, over a great part of the composition range, the liquid crystalline state lies in the unstable region, i.e., is monotropic.

System 20: Figure 11
System 21: Figure 12

DISCUSSION

A. The classification of liquid crystalline modifications in the homologous series.

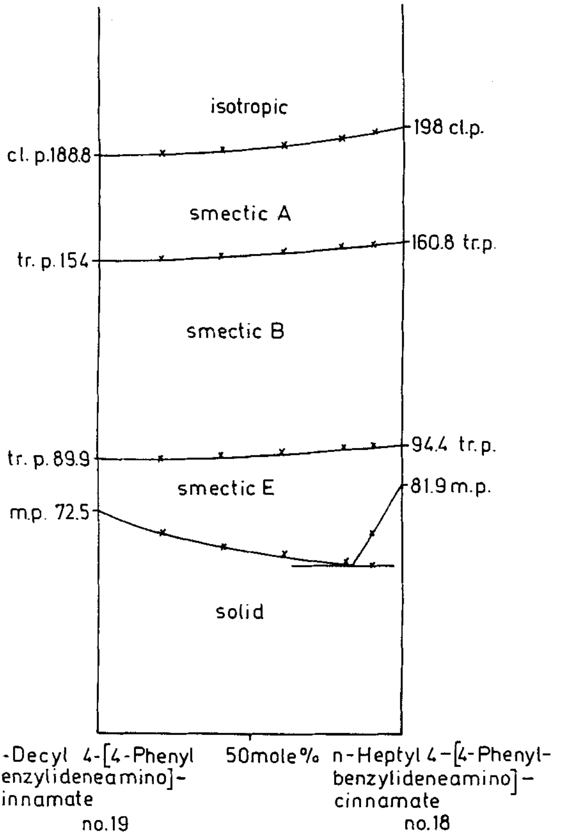


FIGURE 11. System 20

1) *trans*-4-*n*-Alkoxycinnamic acids.

By means of the observation of two uninterrupted series of mixed liquid crystals in System 1, the C_{10} -compound of the *trans*-4-*n*-alkoxycinnamic acid series has the polymorphism SC, N. The regular trends of the transition temperatures[3] over the whole homologous series, combined with this result, show that for the lower members (C_1-C_8) only nematic modifications occur, for C_9-C_{16} the polymorphism is SC, N and for C_{18} a smectic C modification alone occurs.

2) *trans*-4-*n*-Alkoxy-3′-chlorocinnamate acids.

The polymorphism observed in the C_9-compound (dimorphism: SC, N), the monomorphism (SC) for the C_{18} -compound and the trends of the transition temperatures for the homologous series[4] show that the lower members (C_6-C_{12}) exhibit the polymorphism SC, N and the higher members (only C_{16} and C_{18} are known) have only SC phases.

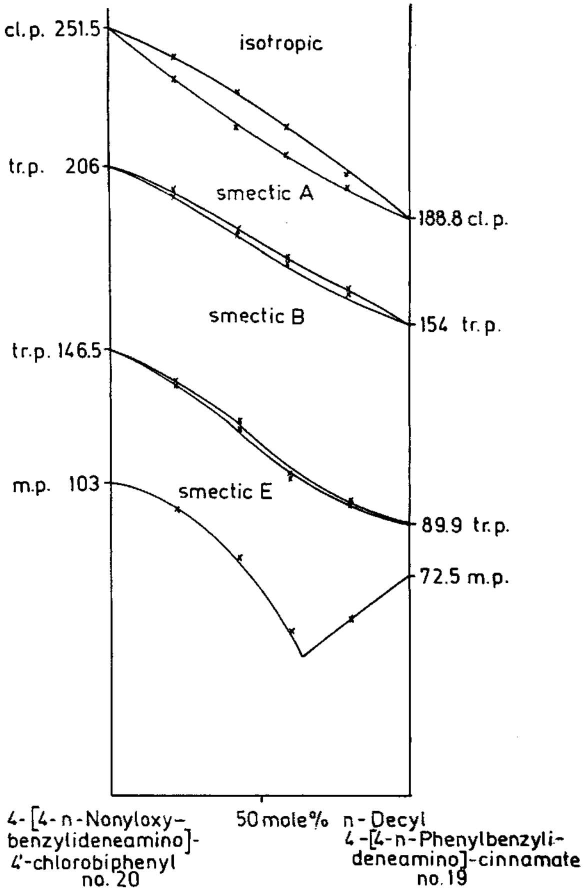


FIGURE 12· System 21

3) 6-*n*-Alkoxy-2-naphthoic acids.

The miscibility relations found for Systems 6 and 7 (chloro-derivatives), for tion temperatures[5] for the homologous series show that the lower members exhibit only nematic modifications, the middle members (C_9-C_{12}) show the dimorphism SC, N and the higher members (only C_{16} and C_{18} are known) have only SC phases.

4) 6-*n*-Alkoxy-5-halogeno-2-naphthoic acids.

The miscibility relations found for Systems 6 and 7 (chloroderivatives), for System 8 and 9 (bromo-derivatives) and for Systems 10 and 11 (iodo-derivatives) and the regular trends of the transition temperatures for each of the homologous series[6] show that for the lower members there occurs monomorphism (N), for the middle members dimorphism (SC, N) and for the higher members monomorphism (SC).

5) 4′-*n*-Alkoxy-3′-halogenobiphenyl-4-carboxylic acids.
The miscibility relations found for Systems 12 and 13 and for Systems 7 and 8 in[1] and the trends of the transition temperatures for the homologous series[7] show that for the lower members (C_3 and C_4) of the series of bromo-derivatives there occurs monomorphism (N), for the middle members (C_5-C_{10}) dimorphism (SC, N) and for the higher members monomorphism (SC). The smectic modification of the 4′-*n*-hexadecyloxy-3′-chlorobiphenyl-4-carboxylic acid also belongs to the type SC.[1] Therefore the 3-chloro-analogues show the same polymorphic behaviour in the homologous series: Members C_2-C_3 exhibit monomorphism (N), members C_4-C_{10} dimorphism (SC, N) and the higher members monomorphism (SC).

6) 4-[4-*n*-Alkoxybenzylideneamino]biphenyls.
Miscibility studies (Fig. 6) of System 14 prove that the C_{10}-compound exhibits the polymorphism SB, SA, N. For the C_5-C_{18} members of the homologous series only one smectic modification was originally reported[8]. However, the melting point of the decyl compound in[8] corresponds to our temperature for the transition SB/SA. It is to be assumed therefore that this is the case for other members of the series, which would then also possess two smectic modifications. It is not perhaps surprising that in the early work of 1955, the SB ⟶ SA transition was taken to be the melting point and the C ⟶ SB transition was overlooked. A reinvestigation of the polymorphism of the whole series seems to be needed, but it can be said that for the C_6 and C_{12} compounds, DTA has revealed that the previously recorded[8] melting points in fact correspond to reversible S-S transitions (probably SB-SA).

7) 2-[4-*n*-Alkoxybenzylideneamino] fluorenes.
System 15 (Fig. 7) shows that the smectic modification of the C_{10}-compound is of the type SA. The polymorphism and the trend of the transition temperatures in the homologous series[8] show that all smectic modifications are of the type SA (lower members: nematic only, middle members: dimorphism SA, N, higher members: monomorphism SA).

8) 2-[4-*n*-Alkoxybenzylideneamino] fluorenones.
The C_{16}-compound exhibits the polymorphism SA, N (Fig. 8). Considering this polymorphism and the transition temperatures in the homologous series[8], the lower members therefore exhibit nematic modifications only, and the higher members (C_7-C_{18}) are dimorphic SA,N.

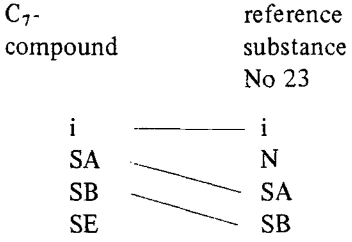
9) 2,7-di-[4-*n*-alkoxybenzylideneamino] fluorenones.

The C_{12}-compound exhibts the polymorphism SC, N (system 17). Considering this polymorphism and the transition temperatures in the homologous series[8], the lower members (C_1-C_4) exhibit nematic modifications only, the middle members (C_5-C_{12}) are dimorphic SC, N and the higher members (C_{16}, C_{18}) exhibit only SC phases.

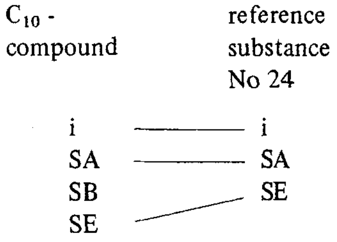
10) *n*-Alkyl [4-phenylbenzylideneamino] cinnamates.

In an earlier investigation[14], the C_2-compound was characterized as a liquid crystalline trimorphic substance of the type SB, SA, N. Higher members first seemed to exhibit smectic dimorphism[9], but new investigations[20] showed that smectic trimorphism occurs. The two high-temperature modifications, by means of texture observations alone, seemed to be SB and SA, agreeing with the results on the C_2-compound. Investigation of the C_7 and C_{10} compounds (Systems 18 and 19) in the following binary combination gives:

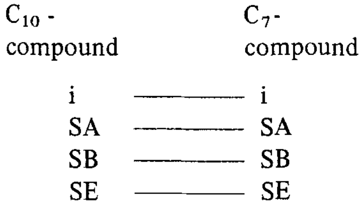
System 18



System 19



System 20



The uninterrupted series of mixed liquid crystals found in the binary mixture (System 18) proves the existence of high temperature smectic modifications A and B for the C_7-compound according to the result above[14]. The miscibility behaviour for the binary mixture (System 19, Fig. 10) shows that the smectic low-temperature-modification of the C_7-compound is of the type E. The existence of the uninterrupted series of mixed liquid crystals of the smectic low temperature states of the binary mixture (System 20) of compounds C_7 and C_{10} (Figure 11) proves that this modification of the C_7 compound is also of the E-type.

The classification of the smectic modifications of the C_7 and C_{10} compounds and the recent observation [20] that the C_2-compound exhibits a *monotropic* SE phase show that lower members (C_2 and C_3) of the homologous series possess the polymorphism SE, SB, SA, N† and the higher members (C_4-C_9) possess the polymorphism SE, SB, SA. The methyl compound (C_1) is dimorphic (SA, N) [20]; very little supercooling occurs and crystallisation takes place before any polymorphic forms of the SA phase can be detected.

11) 4-*n*-Alkyloxybenzylideneamino-4′-chlorobiphenyls.
According to the result of miscibility investigations of system 21 (Fig. 12), the C_9-compound shows the smectic trimorphism SE, SB, SA. Other compounds of the homologous series are not known.

B. Smectic E-modifications. In a previous paper[15] the identification of a new smectic modification of the type E by means of miscibility investigations was described. The diethyl- and dipropyl-esters of *p*-terphenyl-4,4″-dicarboxylic acid exhibit the variant of polymorphism: SE, SA.

The Systems 18, 19, 20 and 21 relating in binary Systems 3 substances with di-*n*-propyl *p*-terphenyl-4,4″-dicarboxylate and one with another reference substance prove the existence of the variant of polymorphism: SE, SB, SA.

This confirms that the new modification E cannot be of the smectic type B. This is in agreement with earlier miscibility investigations of System 19 in Table 18 in [15] showing a heterogeneous region between the B and E-phase areas in the temperature concentration diagram.

All E-modifications show the same type of texture: a paramorphotic fan-shaped texture with concentric arcs [15] or a mosaic texture.

Meanwhile new substances of the Schiff's base type have been synthesized [10, 20] having the smectic polymorphism X, SB, SA with X-phases having the textures described above for the E-modification. It is probable, therefore, that these new modifications X are of the E-type also.

It is interesting to note that at least some of these X-phases are optically biaxial[20], and that X-ray measurements of the E-modifications of the di-alkyl *p*-terphenyl-4,4″-dicarboxylates point to an orthogonal arrangement of the long molecular axes to the planes[21]. One of these terphenyl esters has recently[23] been proved to have an orthorhombic cell in the smectic layers, and this would imply an optically biaxial behaviour. However, optically uniaxial properties are found in this case[21]. This could be explained in the following way: whereas within the plane of a smectic layer the molecules lie in an orthorhombic array, the pos-

---

† The SE phase of the propyl ester is also monotropic [20].

sibility of rotational disorder from one layer stacking to the next could produce an overall uniaxial symmetry.

References

1. Communication No. 19 of this series: Demus, D., Kunicke, G., Neelsen, J. and Sackmann, H. Z. phys. Chem. **255**, 71 (1974).
2. Sackmann, H. and Demus, D.: Mol. Cryst. and Liquid Cryst. **21**, 239 (1973).
3. Gray, G.W. and Jones, B.: J. Chem. Soc. (London) **1954**, 1467.
4. Gray, G.W., Jones, B. and Marson, F. J. Chem. Soc. (London) **1956**, 1417.
5. Gray, G.W. and Jones, B.: J. Chem. Soc. (London) **1954**, 683.
6. Gray, G.W. and Jones, B.: J. Chem. Soc. (London) **1955**, 236.
7. Gray, G.W., Jones, B. and Marson, F.: J. Chem. Soc. (London) **1957**, 393.
8. Gray, G.W., Hartley, J.B., Ibbotson, A. and Jones, B.: J. Chem. Soc. (London) **1955**, 4359.
9. Gray, G.W. and Harrison, K.J.: Mol. Cryst. and Liquid Cryst. **13**, 37 (1971).
10. Gray, G.W. and Harrison, K.J.: Chem. Soc., Faraday Division Symposium No **5**, 54 (1971).
11. Demus, D. and Sackmann, H.: Z. phys. Chem. **222**, 127 (1963).
12. Sackmann, H. and Demus, D.: Z. phys. Chem. **222**, 143 (1963).
13. Pelzl, G., Demus, D. and Sackmann, H.: Z. phys. Chem. **238**, 22 (1968).
14. Demus, D. and Sackmann, H.: Z. phys. Chem. **238**, 215 (1968).
15. Demus, D., Kölz, K.-H. and Sackmann, H.: Z. phys. Chem. **252**, 93 (1973).
16. Arnold, H., Demus, D. and Sackmann, H.: Z. phys. Chem. **222**, 15 (1963).
17. Sackmann, H. and Demus, D.: Mol. Cryst. **2**, 81 (1966).
18. Sackmann, H. and Demus, D.: Fortschr. chem. Forsch. **12**, 349 (1969).
19. Demus, D.: Wiss. Z. Univ. Halle **21** (3), 41 (1972).
20. Coates, D., Harrison, K.J. and Gray, G.W.: Mol. Cryst. and Liquid Cryst. **22**, 99 (1973), and results to be published.
21. Diele, S., Brand, P. and Sackmann, H.: Mol. Cryst. and Liquid Cryst. **17**, 163 (1972).
22. Smith, G.W., Gardlund, Z.G. and Curtis, R.J.: Mol. Cryst. and Liquid Cryst. **19**, 327 (1973).
23. Diele, S.: Phys. stat. sol. (a) **25**, K183 (1974).