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

Identification of the Liquid Crystal Phases of some Chiral Schiff Bases

Jean Billard [a] [b] , Anders Dahlgren [a] , Kurt Flatischler [a] , Sven T. Lagerwall [a] & Bengt Otterholm [b] [a]

[a] Department of Physics and Department of Organic Chemistry, Chalmers University of Technology, S-412 96, Göteborg, Sweden

[b] Laboratoire de Physique de la Matière Condensée (Equipe de Recherche assoiée au C.N.R.S. no. 542), Collège de France, 75231, Paris, Cédex 05, France

Version of record first published: 28 Mar 2007.

To cite this article: Jean Billard , Anders Dahlgren , Kurt Flatischler , Sven T. Lagerwall & Bengt Otterholm (1986): Identification of the Liquid Crystal Phases of some Chiral Schiff Bases, Molecular Crystals and Liquid Crystals, 135:3-4, 265-282

To link to this article: http://dx.doi.org/10.1080/00268948608084814

Mol. Cryst. Liq. Cryst., 1986, Vol. 135, pp. 265-282
0026-8941/86/1354-265/$20.00/0

Printed in the United States of America

Identification of the Liquid Crystal Phases of some Chiral Schiff Bases

JEAN BILLARD†, ANDERS DAHLGREN, KURT FLATISCHLER, SVEN T. LAGERWALL and BENGT OTTERHOLM‡

Department of Physics and Department of Organic Chemistry‡, Chalmers University of Technology, S-412 96 Göteborg, Sweden

(*Received February 12, 1985; in final form July 13, 1985*)

The mesophases of eleven chiral Schiff bases are identified by miscibility examinations, using the contact method. Some of these compounds exhibit medium pitch (2-3 μm) chiral smectic C mesophases with left-handed twist which are thermodynamically stable near room temperature. Some binary mixtures having thermodynamically stable ferroelectric (C*) state at room temperature are described.

1. INTRODUCTION

The existence of a spontaneous electric polarization in chiral tilted smectics[1] and the possibility to use this phenomenon to elaborate a bistable device having fast dynamics[2-4] have recently stimulated research on liquid crystals exhibiting a chiral smectic C phase at low temperature. The previously published low-melting compounds of the class C* are rare, the first one dating from 1971, 2-chloro-1,4-

---

†Permanent Address: Laboratoire de Physique de la Matière Condensée (Equipe de Recherche associée au C.N.R.S. no. 542), Collège de France, 75231 Paris Cédex 05, France

bis-[S-4-(6-methyl)-octyloxybenzylidene]-phenylene diamine,[5] with the phase transitions†

$$\mathrm{X}\ 29\ \mathrm{C}^*\ 94.4\ \mathrm{N}^*\ 146.5\ \mathrm{L}\ {}^{12}.$$

A subsequent example is 4″-hexyloxyphenol 4-(2-methyl)-butylbiphenyl-4′-carboxylic ester (C-6)[6]

$$\mathrm{X}\ 68.8\ \mathrm{C}_l^*\ 80.2\ \mathrm{N}_l^*\ 163.5\ \mathrm{L}$$

which together with the homologs C-4, 5, 7, 8 and 10 gives a six-component mixture[6] with transitions

$$\mathrm{X}\ 39.4\ \mathrm{C}_r^*\ 74.3\ \mathrm{N}_r^*\ 162.2\ \mathrm{L}$$

(the handedness given for these two compounds stems from our observations). Other examples are the d-4-(methylbutoxy)phenyl ester of 4-decyloxybenzoic acid[22]

$$\mathrm{X}\ 44.0\ \mathrm{C}^*\ 53.8\ \mathrm{A}\ 67.0\ \mathrm{L}$$

and the S-4-(2-methyl)butyl-resorcylidene-4′-alkylanilines[7,8] (compounds *2-m* of Table I; *MBRA series*, cf. the table for transitions).

In a more recent paper Hallsby et al. have added some new members to this series and described the corresponding S-4-(6-methyl)-octyl-resorcylidene-4′-alkylaniline (compounds *1-m*, Table I,—*MORA series*) and, in addition, the 2-chloro-1,4-bis-4-[S-(2-methyl)-butyl-resorcylidene -phenylenediamine, cf. Table I (compound *3*). Two further compounds, (*4-4*, *4-9*, yet unpublished), by the same authors have been listed in Table I. In the resorcylidene compounds the hydroxy group in ortho position stabilizes the anil linkage. We here report the phase identification of the liquid crystals as exhibited by the above mentioned compounds. In this introduction we also finally want to draw attention to several interesting new cases of low-melting ferroelectric compounds by Pavel et al.,[23] by Goodby and Leslie[24] and by Keller[29] in recent publications.

---

†Transition temperatures in degrees Celsius; X and L are our phase designations for crystalline and isotropic liquid, respectively.

2. GENERAL OBSERVATIONS

The compounds were studied with a Mettler TA3000 differential scanning calorimeter and observed with a polarizing microscope having a Mettler FP52 heating attachment. The enthalpy changes at the transitions were taken at runs with ascending temperature (2 °C/min).

With the exception of *2-4* and *4-4* (Table I) these yellow compounds exhibit thermodynamically stable mesophases. The cholesteric phases of *1-4* and *3* are highly fluid and exhibit vivid colours between polarizers due to the dispersion of the apparent rotatory power. The cholesteric phase of *3* reflects light in the visible: green at 172 °C, blue at higher temperature and red at lower temperature. On top of the cholesteric phase both the blue phases (BPI, II) and the blue fog appear. Supercooling can be observed at the transitions L-BPII, BPII-BPI and BPI-N*. The smectic A phase textures of (*2-8, 2-12, 4-4* and *4-9* are focal conic or homeotropic. The smectic C phases appear as striated or broken focal conics if between untreated glasses or with colours due to the apparent rotatory power dispersion if between glass slides coated with polysilanes,[11] demonstrating that the smectic twist axis is preferably perpendicular to the glass surfaces in the latter case.

In the supercooled twisted smectic I phase of *1-12* Schlieren texture is seen between untreated glasses and strong rotatory dispersion colours between treated glass plates similar to those of the C* phase.

3. IDENTIFICATION OF THE PHASES

In order to identify the nature of a certain liquid crystal phase a continuous miscibility is required with a second phase of the same symmetry. (Chirality and reflection symmetry play a special role in this context.) The miscibility was found by establishing binary isobaric phase diagrams from microscopic observations of contact preparations.[13] The reference substances used as bases for phase identifications are given in Table II below.

We first discuss the MORA series

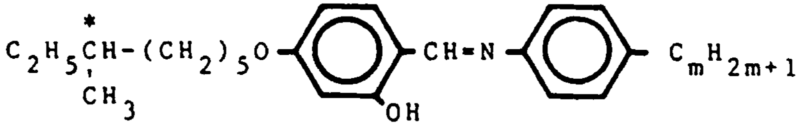
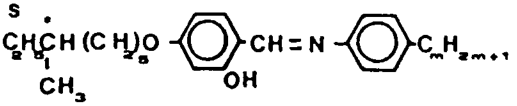


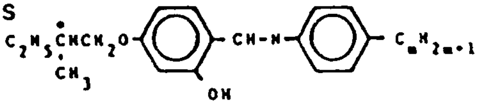
TABLE I

Studied compounds



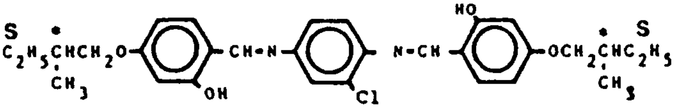
(1) (MORA series)

Number	m	X		S_3	I_i^*		C_i^*		N_i^*		L
1-4	4	·				38.2	·	66.1	·	70.5	·
						13.4		*2.1*		1.2	
1-6	6	·				18.8	·			80.6	·
						10.0				*6.44*	
1-8	8	·				20.4	·			85.7	·
						28.1				*9.29*	
1-10	10	·	25.3		(.16.6)		·			87.1	·
			30.1		(*0.14*)					*8.68*	
1-12⁺	12	·	36.7	(.24.8)	(.26.6)		·			86.5	·
			44.9							*9.06*	



(2) (MBRA series)

Number	m	X		C_i^*	A	N_i^*	L
2-4	4	·	51.6	(.23.6)		(.36)	
			7.57				
2-8	8	·	35.6	·50	·	56.8	·
			15.0	~0		*4.00*	
2-12	12	·	45.4	(.34.8)	·	63.1	·
			· *42.5*			*6.3*	

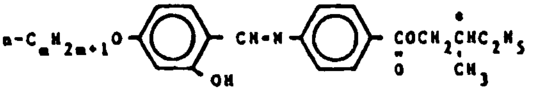


(3)

Number	X		C_i^*	N_i^*		BPI	BPII	L
		146.6	(141.1)		175.4	· 175.7	· 176.2	·
3	·	*27.4*	*0.41*	·		*0.78*		

The four phase diagrams of the compounds *1-4*, *1-6; 1-6*, *1-8; 1-8*, *1-10* and *1-10*, *1-12* (Figure 1) establish that the five studied compounds of the series *1* have the same stable smectic phase. In the phase diagram of the mixtures of the compounds *1-10* and *1-12* (Figure 1, right) the smectic-liquid spindle is almost reduced to a horizontal straight line. The cholesteric phase of *1-4* is identified by its total miscibility in this phase with the reference substance R1 (cf. Table II) shown in Figure 2. The chiral smectic C and I phases of the 1-12 compound are identified by the phase diagram of its mixtures with R2 (Figure 3) which exhibits smectic C and I[16] phases. By analogy one concludes that the lower smectic phase of *1-10* is smectic I.

TABLE I (continued)



(4)

		X		A	L
4-4	4	·	87.6	(· 79.8)	
			19.6	· 85.0	
4-9	9		82.5	*3.9*	
			20.5		

In this Table are given the temperatures for the transitions in degrees Celsius and (in italics) the molar enthalpy changes in kJ/mole. The values in parenthesis concern monotropic or virtual transitions. Our phase designations are: X, N, L, A, C, I for crystal, nematic, (isotropic) liquid, smectic A, C and I respectively. The letter *S* (for sinister) indicates the absolute molecular configuration.[10] The letter *l* as index indicates a left-handed twist.

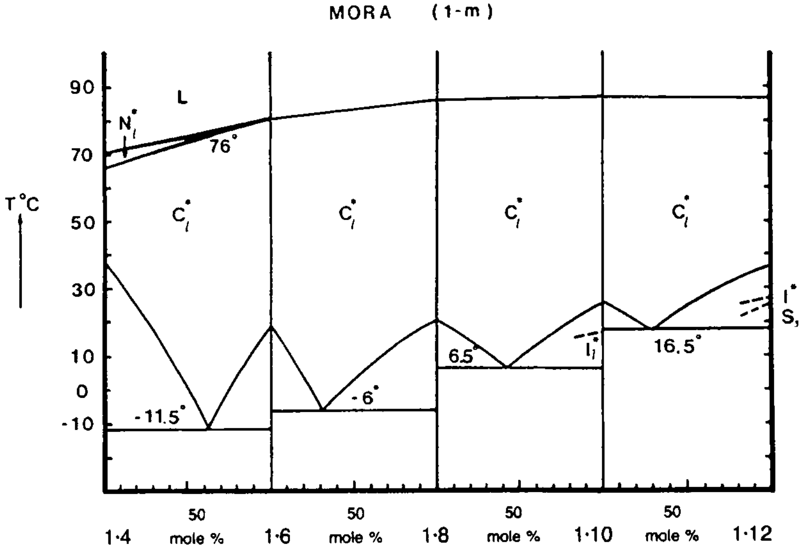


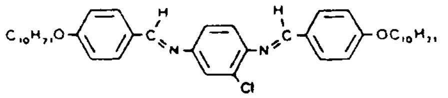
FIGURE 1 Four binary phase diagrams of the five studied compounds for the series *1*-m (see Table I). The last two of these compounds have monotropic smectic I* phases (below the C* phases). The solubility curves in the C* state are calculated with Le Chatelier-Schröder relations[25,26] from the measured melting enthalphy changes.

TABLE II

Reference substances

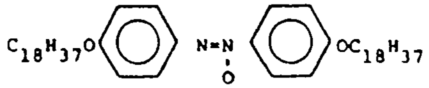
Ref. 1 2-chloro-1,4-bis(4'-n- decyloxybenzylidene) phenylene diamine

× 66 C 112.5 N 166.5 L



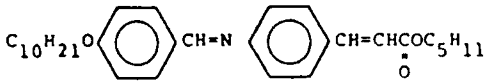
Ref. 2 4,4'-di-n-octadecyloxy-azoxybenzene [15] [16]

× 94.2 I 99 C 115.3 L



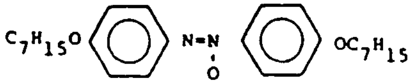
Ref. 3 n-pentyl 4-n-decyloxybenzylidene-4'-aminocinnamate [17]

× 76.4 I 98.8 C 106.8 A 136.4 L



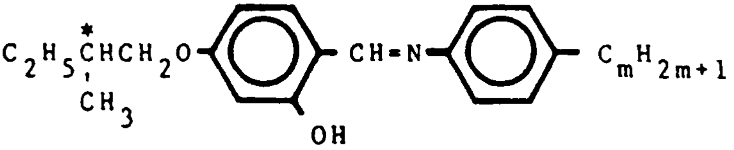
Ref. 4 4,4'-di-n-heptyloxyazoxybenzene [18]

× 74.4 C 95.4 N 124.2 L



In the case of *1-12* we found two monotropic smectic phases below the C phase as also found by Brand and Cladis.[28] The first is the already mentioned I* phase with only a small existence range. The second is a phase (S_3), the nature of which we have not been able to identify by miscibility. Both phases are ferroelectric as easily seen by the response to an applied low-voltage DC electric field. The I* phase is fairly subtle whereas the transition I→S_3 is more dramatic due to the unwinding of the helix at the transition.

The identifications are similar in the MBRA series.



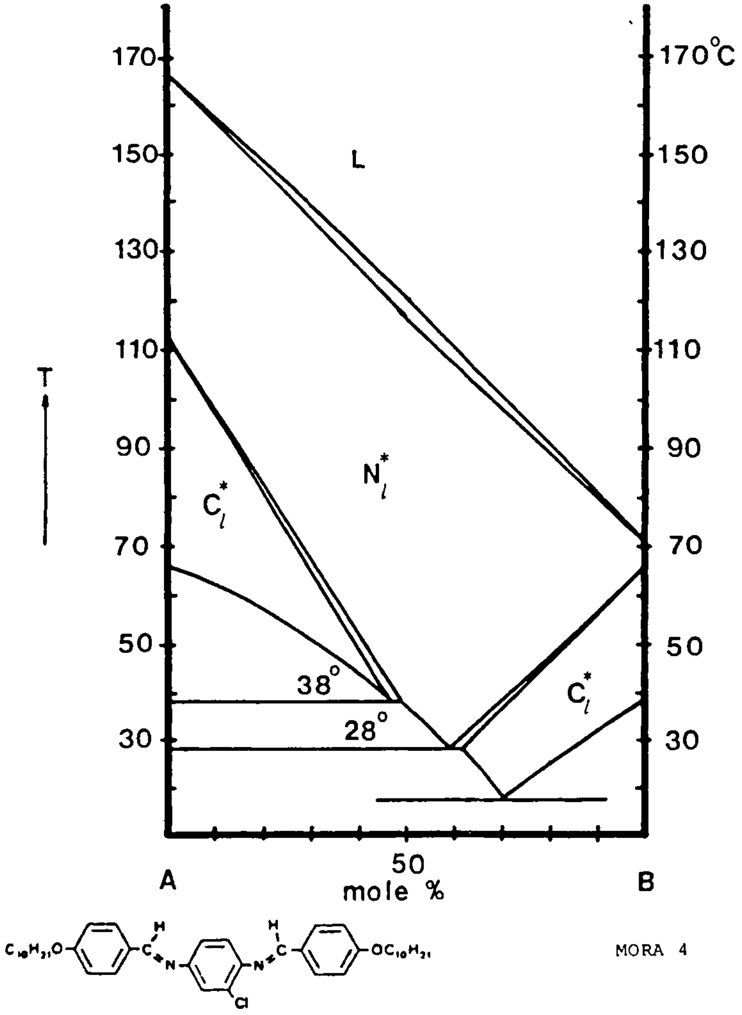


FIGURE 2 Identification of the N* phase of *1-4* (B) from total miscibility with 2-chloro-1,4-bis(4′-n-decyloxybenzylidene)-phenylene diamine (A) in the nematic state.

The smectic A phase of *2-12* is ascertained from the binary phase diagram of its mixtures with R3 shown in Figure 4. The compounds *1-12* and *2-12* show an observable region of miscibility in the C* state, which can be used to identify a virtual A-C* transition in the pure compound *2-12*, cf. Figure 5. The two thermodynamically stable smectic phases of *2-8* are identified respectively as A by the mixture with *2-12* (Figure 6) and as C* by the mixture with *1-12* (Figure 7). The

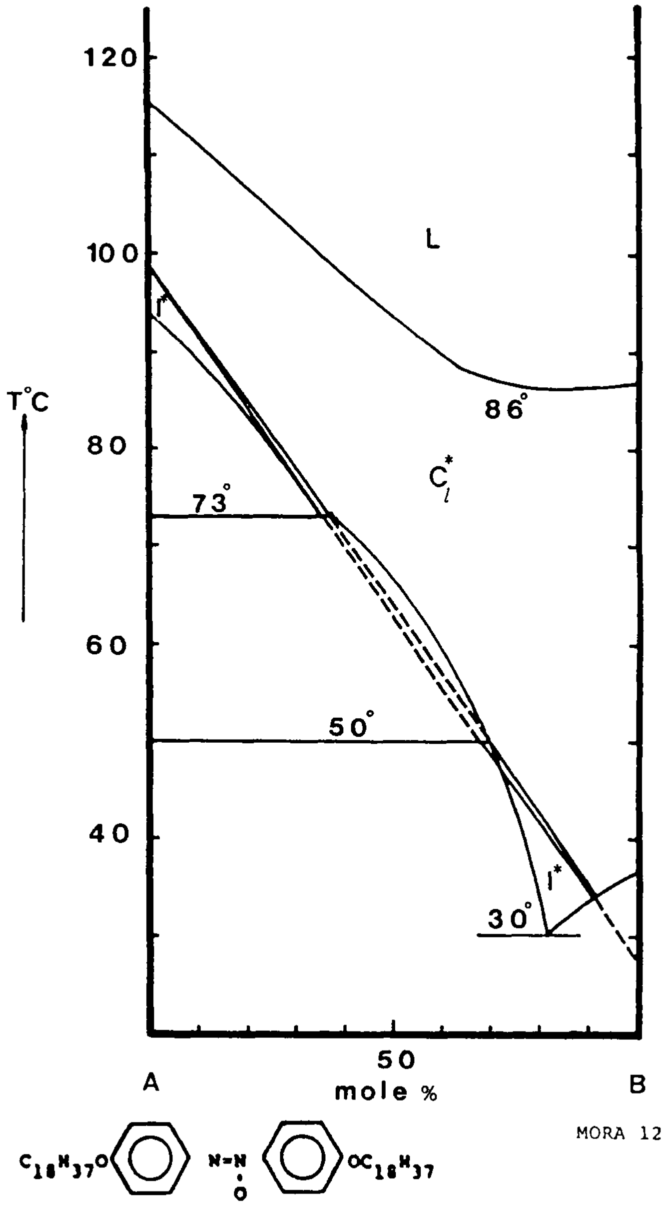


FIGURE 3 Total miscibilities in the smectic C and I states of *1-12* (B) with 4,4'-di-n-octadecyloxy-azoxybenzene (A).

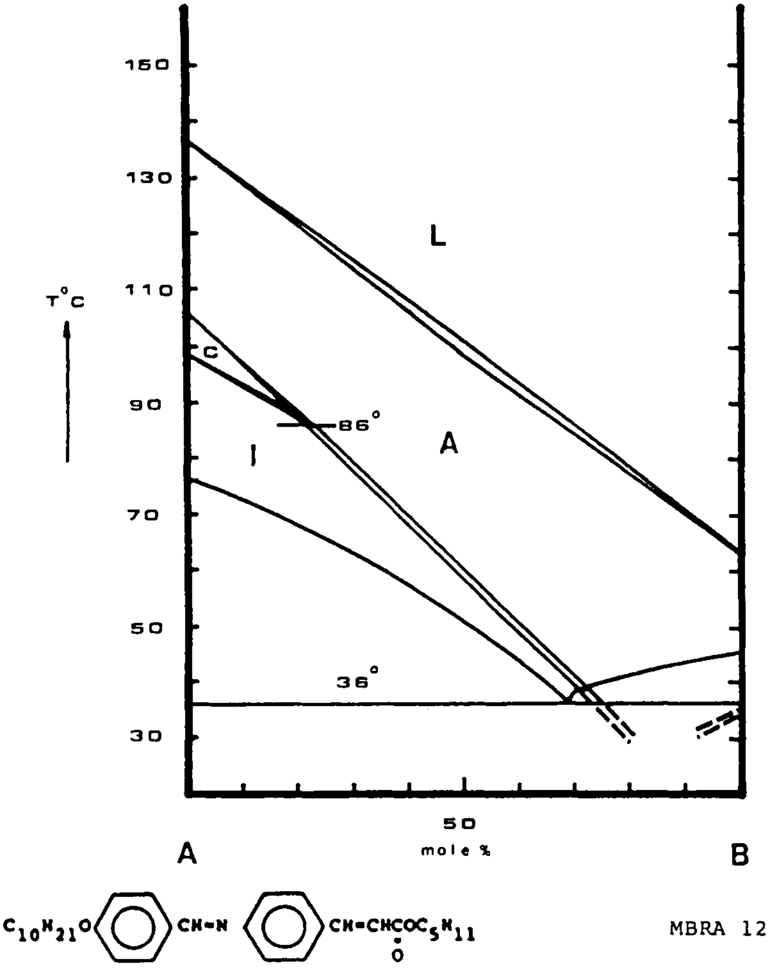


FIGURE 4 Total miscibility in the smectic A state of *2-12* (B) with n-pentyl 4-n-decyloxybenzylidene-4'-amino-cinnamate (A).

virtual C*-N* and N*-L transitions of *2-4* are obtained from the binary phase diagram of its mixtures with *1-4* (Figure 8).

The monotropic C* phase and the N* phase of the compound *3* are identified by the phase diagram of its mixtures with R4, as seen in Figure 9.

As, finally, for the *4-m* compounds, the smectic A phase of *4-9* is

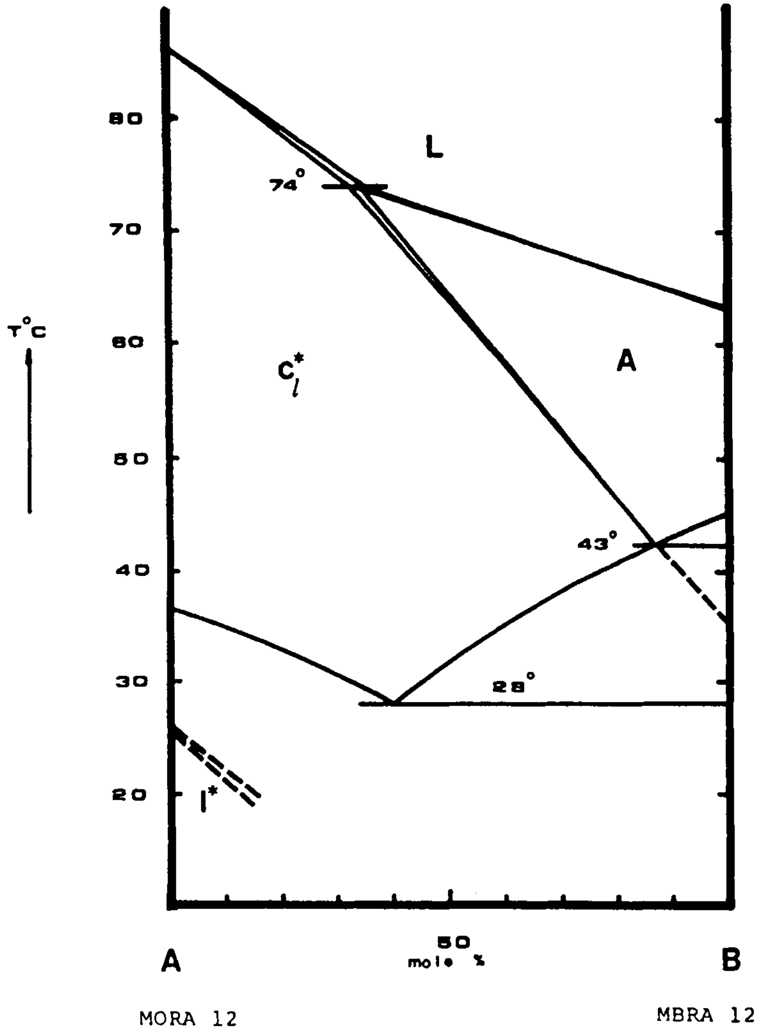


FIGURE 5 Identification of the monotropic C* phase of *2-12* (B) from the total miscibility in the chiral smectic C state with *1-12* (A).

identified by the phase diagram in Figure 10 of its mixtures with *2-12*. The nature of the monotropic A phase of its homolog *4-4* is then ascertained from the phase diagram of the mixtures with *4-9*, cf. Figure 11.

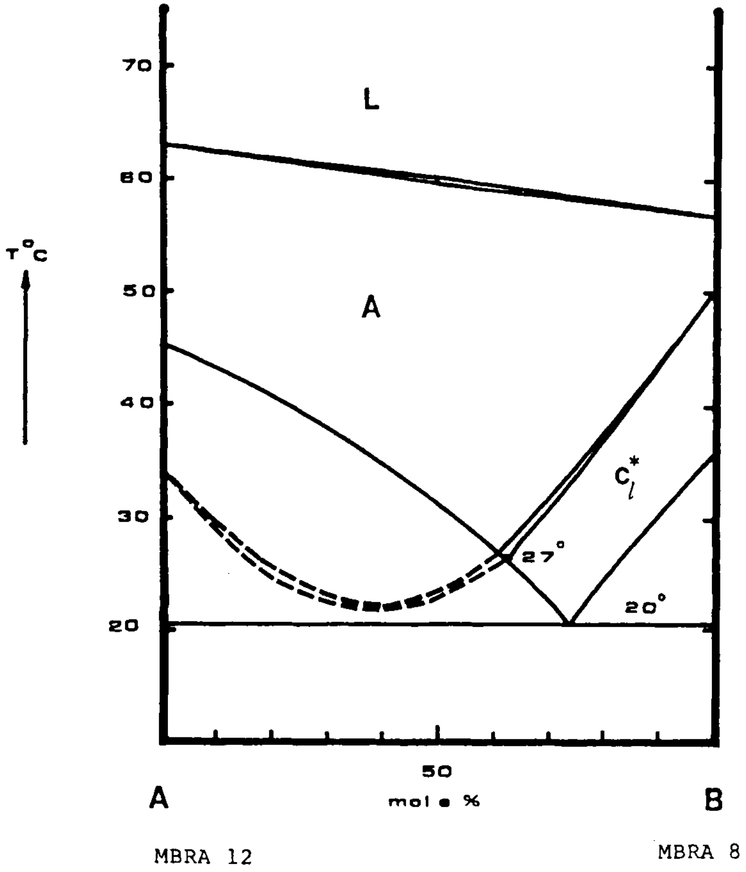


FIGURE 6 Total miscibility in the smectic A state of *2-8* (B) and *2-12* (A).

4. TWIST SENSE

The handedness of the twist in the chiral liquid crystals was deduced from the observations of the displacement of the isochromatic lines versus the rotation of the analyzer in contact preparations of the binary mixtures, due to the existing gradients in composition.[19]

The results are indicated in Table I as well as in the figures. The index *l* indicates a left-handed twist. The smectic I mixtures rich in *1-12* (Figure 3) exhibits colours due to the dispersion of the apparent rotatory power but the variations of concentration are too small to allow the deduction of the twist sense of the smectic I* phase in this case. All the C* mixtures of the studied compounds of the series *1* (Figure 1) appear as striated focal conics. No untwisted C* phase

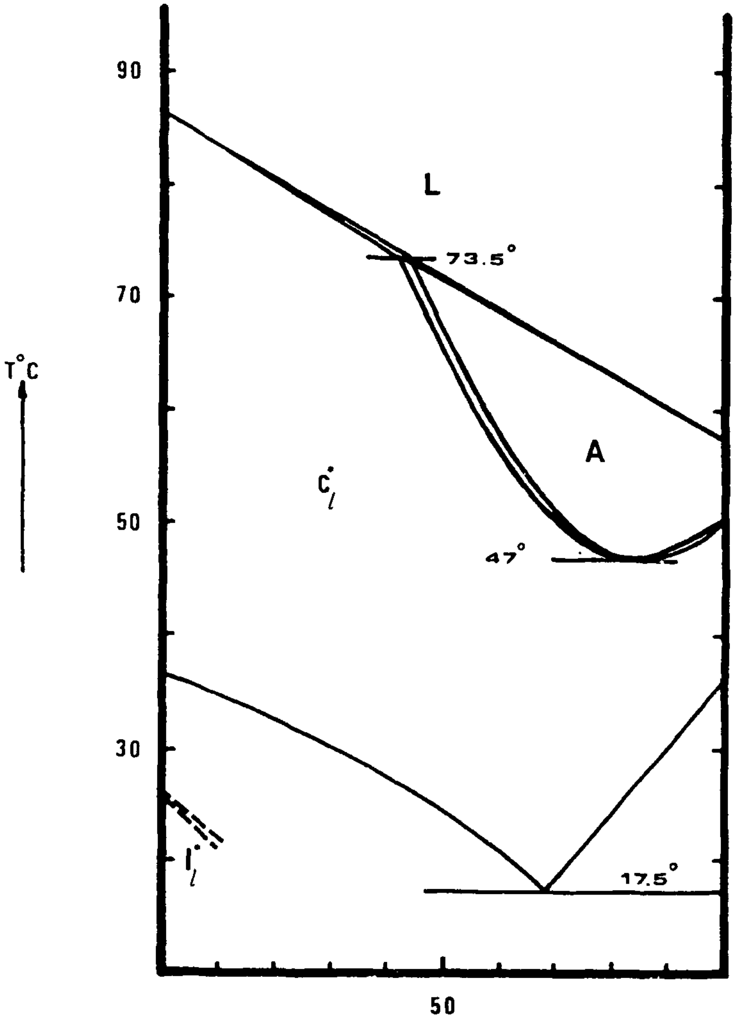


FIGURE 7 Total miscibility in the chiral smectic C state of *2-8* (B) and *1-12* (A).

could be obtained in these binary mixtures. Consequently,[20] the C* phases of *1-4*, *1-6*, *1-8*, *1-10*, and *1-12* all have the same left-handed twist sense. (The corresponding odd-numbered compounds have not been synthesized.) Similar observations can be made on the C* mixtures of Figures 5 and 7 and on the C* and N* mixtures of Figure 8.

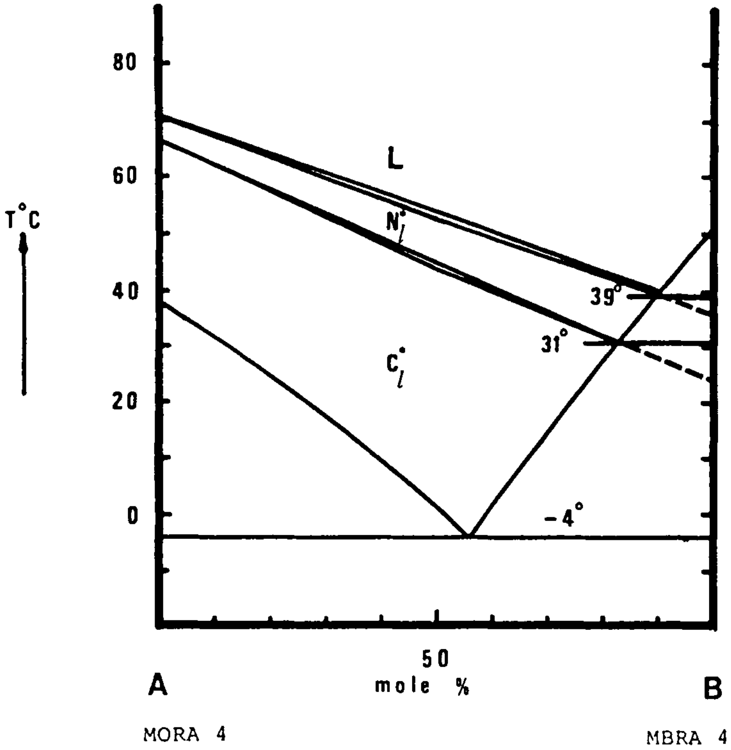


FIGURE 8 Binary phase diagram of the mixtures of *2-4* (B) and *1-4* (A), identifying two virtual transitions C*– and N*– in *2-4*.

The pitches of the C* phases of the studied compounds of the series *1* (at 50 °C) were estimated from the distances between the striations in the focal conics (observed with Zeiss UD 40 × 0.65 objective), cf. Table III. (The temperature dependence of the pitch cannot be obtained conveniently by this method.) The pitch values obtained here are somewhat lower than those measured on diffraction patterns.[21] The pitch of the twisted smectic C phase of *2-8* has been previously measured.[27]

TABLE III

Approximate pitch in the C* phase of the compounds of the series *1* (at 50° C)

Number	*1-4*	*1-6*	*1-6*	*1-10*	*1-12*
Pitch (μm)	1.8	2.4	2.7	3.5	4.3

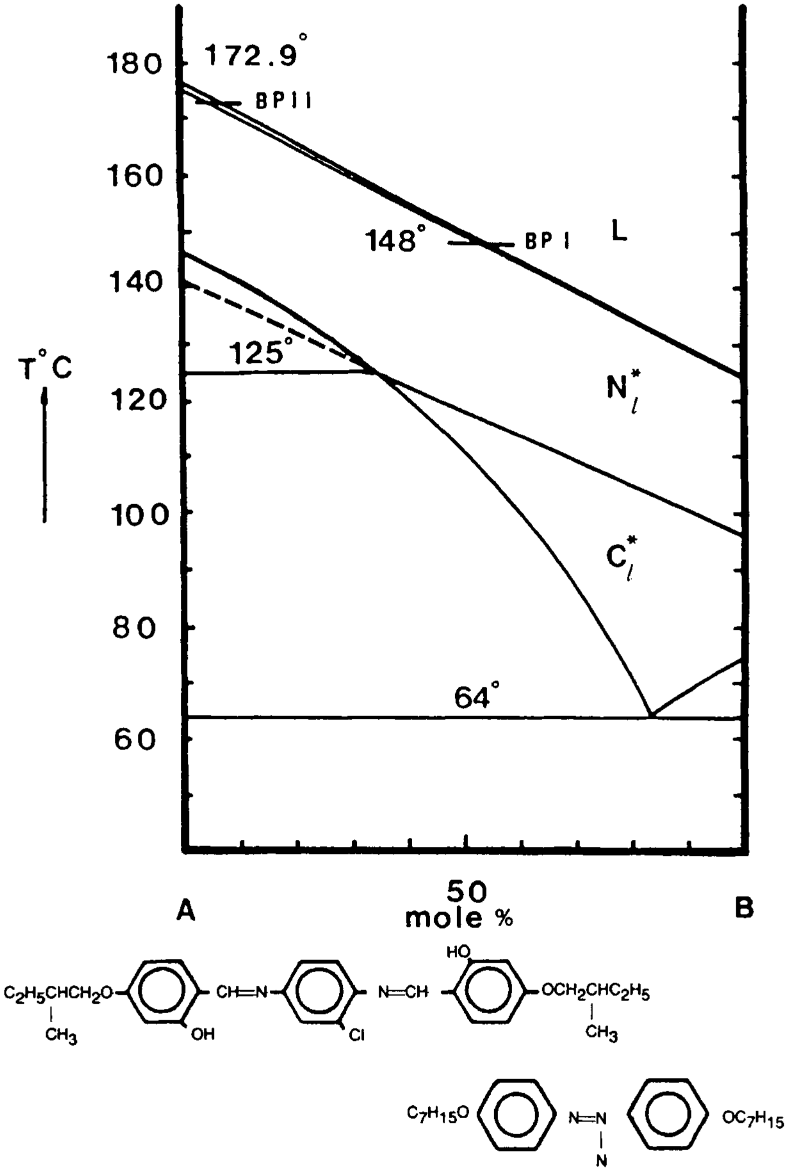


FIGURE 9 Total miscibilities in the chiral smectic C and nematic states of *3* (A) and 4,4′-di-n-heptyloxy-azoxy-benzene (B).

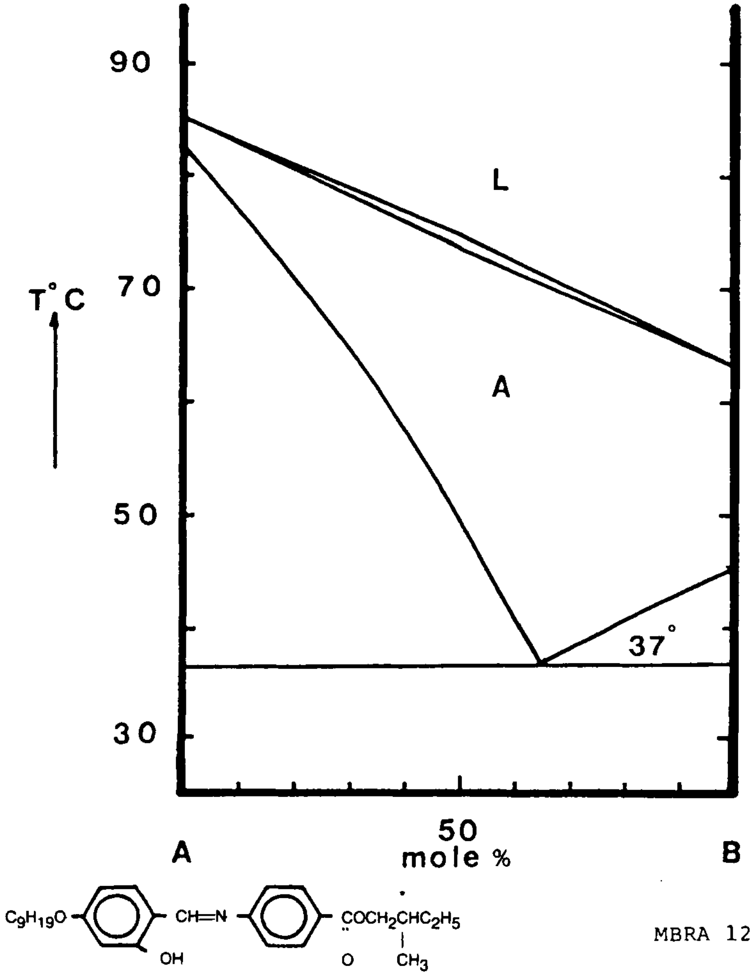


FIGURE 10 Total miscibility in the smectic A state of *4-9* (A) and *2-12* (B).

5. DISCUSSION

Even members of the MORA series form nearly ideal solutions. Also, we see from Figure 8 (MORA 4 with MBRA 4) and Figure 5 (MORA 12 with MBRA 12) that corresponding members of the series may mix ideally in the N* and even in the A phase although the chiral side chain of MORA is considerably longer than in MBRA. In the two mentioned cases the C* phases can be in equilibrium with a eutectic, particularly pronounced in the 4,4 case with a calculated eutectic temperature of −4 °C.

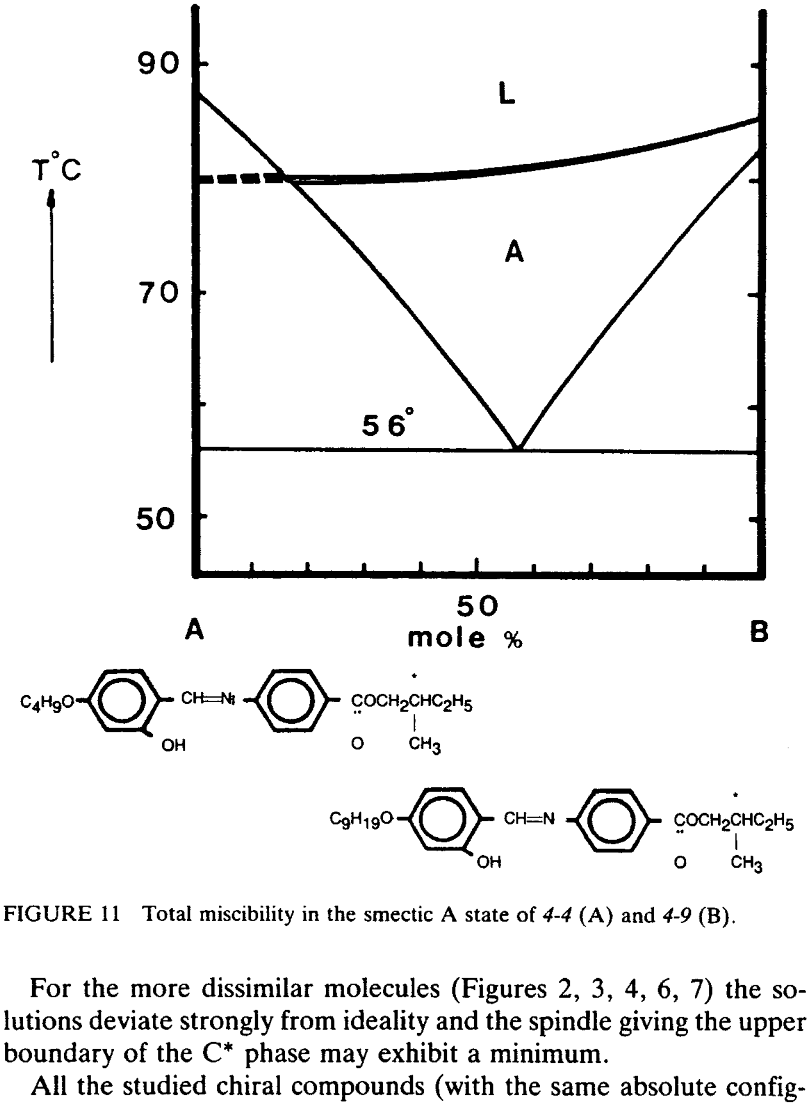


FIGURE 11 Total miscibility in the smectic A state of *4-4* (A) and *4-9* (B).

For the more dissimilar molecules (Figures 2, 3, 4, 6, 7) the solutions deviate strongly from ideality and the spindle giving the upper boundary of the C* phase may exhibit a minimum.

All the studied chiral compounds (with the same absolute configuration) have a thermodynamically stable or virtual smectic C mesophase of left-handed twist. One compound (*1-6* or MORA-6) is a room temperature ferroelectric, some of the other compounds have this phase (C*) at slightly higher temperature. Binary (and, of course, higher) mixtures of compounds of the series *1* can be made with the C* state extending well below room temperature; the calculated eutectics are given in Table IV. For the compounds of the series *1* the twist pitch increases with the length of the alkyl side chain.

TABLE IV

Calculated eutectic binary mixtures

Components	Temperature (°C)	Composition (mole %)
1-4, *1-6*	−11.5	37, 63
1-6, *1-8*	−6	68, 32
1-8, *1-10*	6.5	56, 44
1-10, *1-12*	16.5	69, 31
1-4, *2-4*	−4.4	44, 56

6. CONCLUSION

The homologous MORA series (*1*) exhibits stable C* phases together with some monotropic I* phases; the MBRA series (*2*) stable or monotropic A phases together with stable C* phases. Both series *1* and *2* are able to give compounds with C* phases near or at room temperature. Some binary mixtures (Figures 1, 6, 7 and 8) are in a thermodynamically stable C* state (ferroelectric) in a reasonably broad interval around room temperature. Whereas it is true that the MORA compounds themselves have very low polarization and thus are unsuitable for applications, their excellent broad-band C* phase stability can be retained when making the appropriate structural changes for achieving higher P value and higher chemical stability in forthcoming ferroelectric substances.

Acknowledgments

This work was supported by the National Swedish Board for Technical Development. The authors are grateful to Prof. J. Jacques and Dr. L. Liébert and their co-workers for providing several of the utilized reference substances.

References

1. R. B. Meyer, L. Liébert, L. Strzelecki and P. Keller, *J. Physique Lett.*, **36** L, 69 (1975).
2. N. A. Clark and S. T. Lagerwall, Liquid Crystals of One- and Two-Dimensional Order (W. Helfrich and G. Heppke, eds.) Springer, Berlin, 1980), pp. 222–27.
3. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
4. N. A. Clark, M. A. Handschy and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.*, **94**, 213 (1983).
5. W. Helfrich, *S. Oh. Mol. Cryst. Liq. Cryst.*, **14**, 289 (1971).
6. G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst.*, **37**, 189 (1971).
7. B. I. Ostrovskii, A. Z. Rabinovich, A. S. Sonin, E. L. Sorkin, B. A. Strkuov and S. A. Taraskin, *Ferroelectrics*, **24**, 309 (1980).

8. D. F. Aliev, M. A. Aslanov, M. V. Loseva and N. I. Chernova, *Fiz. Tverdogo Tela*, **24**, 3179 (1982); *Sov. Phys. Solid State*, **24**, 1804 (1982).
9. A. Hallsby, M. Nilsson and B. Otterholm, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 61 (1982).
10. R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).
11. F. J. Kahn, *Appl. Phys. Lett.*, **22**, pp. 386-388 (1973).
12. As we have found, the C* phase of this compound is, in reality, only stable down to 43 °C but easily supercools. According to our observations the transitions are at X 43.6 C_t^* 96.4 N_t^* 147.2 L.
13. L. Kofler and A. Kofler, Thermomikromethoden, *Verlag Chemie*, Weinheim (1956).
14. T. R. Taylor, J. L. Fergason and S. L. Arora, *Phys. Rev. Lett.*, **24**, 359 (1970).
15. H. Arnold, J. Jacobs and O. Sonntag, *Z. Phys. Chem.*, **240**, 178 (1969).
16. H. Sackmann, Liquid Crystals of One- and Two-Dimensional Order, (eds. by W. Helfrich and G. Heppke, Springer, Berlin, 1980) pp. 19–30.
17. D. Demus, H. Sackmann, G. Kunicke, G. Pelzl and R. Salffner, *Z. Naturforsch*, **23a**, 76 (1968); L. Richter, N. K. Sharma, R. Skubatz, D. Demus, H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **80**, 195 (1982).
18. D. Demus and H. Sackmann, *Z. Phys. Chem.*, **222**, 127–42 (1963).
19. N. Isaert, B. Soulestin and J. Malthète, *Mol. Cryst. Liq. Cryst.*, **37**, 321 (1976).
20. J. Billard, C. R. Acad, *Sc. Paris* **274B**, 333 (1972).
21. K. Skarp, K. Flatischler, K. Kondo, Y. Sato, K. Miyasato, K. Takezoe A. Fukuda and E. Kuze, *Jap. J. Appl. Phys.*, **22**, 566 (1983).
22. M. V. Loseva, B. I. Ostrovskij, A. Z. Rabinovich, A. S. Sonin, B. A. Strukov and N. I. Chernova, *JETP Lett.*, **28**, pp. 374-78 (1978).
23. J. Pavel, M. Glogarová, D. Demus, A. Mädicke and G. Pelzl, *Cryst. Res. & Technol.*, **18**, 915 (1983).
24. J. W. Goodby and T. M. Leslie, *Mol. Cryst. Liq. Cryst.*, **110**, 175 (1984).
25. H. Le Chatelier, C. R. Acad, *Sc. Paris*, **100**, 50 (1885).
26. I. Schröder, *Z. Phys. Chem.*, **11**, 449 (1983).
27. D. F. Aliev and M. A. Aslanov, *Fiz. Tverd. Tela*, **23**, 3712, (1981); *Sov. Phys. Solid State*, **23**, 2160 (1981).
28. H. R. Brand and P. E. Cladis, personal communication.
29. P. Keller, in *Ferroelectrics*, **58/59** special issue on Ferroelectric Liquid Crystals (1984).