R. Eidenschink

Properties of Dyes for Liquid Crystal Displays

Properties of dyes for liquid crystal displays
Abstract: The required properties of dyes acting as guest molecules in liquid crystal matrices such as high order parameters, high absorption coefficients, high solubilities and good stabilities are outlined (34 refs.). Particular attention is given to the correlation between dye structure and order parameter.

Introduction

The direction of the orientation of form-anisotropic molecules forming a liquid crystal phase can be influenced by an electric field. If the dielectric constant measured in the direction of the longest molecular axes of the rod-like molecules is larger than the value perpendicular to this direction, the molecules will be oriented with their longest axes parallel to the field[1]. This case of a nematic phase with positive dielectric anisotropy is contrasted by compounds whose molecules have a strong permanent dipole moment perpendicular to the longest axis rendering the dielectric anisotropy negative. The molecules of such a nematic phase, therefore, are orientated perpendicular to the direction of a sufficiently strong electric field[2]. Because of the fact that the optical properties of nematic phases also depend on the direction in space, the aforementioned effect can be exploited for electrooptical devices. These so-called liquid crystal displays have become indispensible elements for watches, pocket calculators, electronic games, data screens etc. The technology currently used almost exclusively is the twisted nematic cell (TNC)[3,4], which requires polarizer foils for each of the two glass plates between which the oriented nematic phase is sandwiched.

A quite different method of influencing the intensity of light passing through liquid crystal layers is based on an idea of *G. H. Heilmeier*[5]. The order in a nematic phase causes the molecules of a dye dissolved in it to orient parallel to each other. Assuming that the transition moment for the absorption of visible light is parallel to the director $\vec{n}$, i.e. the preferred direction of the longest axes of the nematic molecules, light polarized parallel to $\vec{n}$ will be absorbed, as shown in Fig. 1a. When the molecules are oriented perpendicular to the glass plates of the cell by an electric field, absorption will be low, as shown in Fig. 1b. The regions of the display that are in the on-state of the electric field are colorless whilst the ones in the off-state are colored. The reverse situation can be achieved when the same dyes are dissolved in a host with a negative dielectric anisotropy. In practice, displays having a contrast from black to white are required most. Therefore many species of dye molecules covering the whole region of the visible spectrum have to be dissolved.

These different types of *Heilmeier* cells still need a polarizer. *D. L. White* and *G. N. Taylor*[6] have shown that dye molecules arranged in a helix, which can be brought about by doping a nematic host with chiral additives, can absorb unpolarized light effectively. This is due to the fact that the light propagating in two elliptically polarized modes is absorbed by the dyes when the height of the helix is sufficiently small, a low birefrengence value of the host material being advantageous. The planar cholesteric arrangement of the molecules shown in Fig. 2 can be transformed into a homeotropic nematic one in which the transition moments of the dyes are parallel to the radiation direction of light, so that no absorption occurs. A big advantage of the *White-Taylor* cell over TNC is its almost angle-independent contrast. On the other hand, the possibility of multiplexing[7] is limited. The physical backgrounds relevant to display parameters have been elucidated elsewhere[8]. Guest-host technologies include several interesting new approaches, e.g. the double layer cell, which eliminates the need for polarizer foils but which is more difficult to manufacture[9].

In practice, the molecules of the nematic host and the dye cannot be assumed to have a perfect parallel ordering. In consequence, there will be a switching from a deeply colored to a weakly colored state, as is shown by the residual absorption in Fig. 1b. In order to obtain a sufficiently deep color, a minimum of dye with the highest possible absorption coefficient must be dissolved. To prevent the polar dye crystallizing out at the lower temperatures encountered in use, great efforts have been made to synthesize dyes soluble in common nematic compounds of relatively low polar character[10]. Another aspect is the stability of the dyes towards light. These aspects are examined in the following sections. Special emphasis is given to the orientation of the dye molecules in nematic matrices, the understanding of which is a precondition for the more accurate synthesis of new species with high order parameters.

Conditions for high order parameters

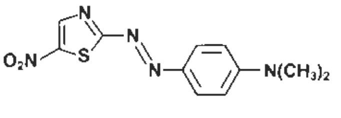
A good contrast of guest-host displays implies high dichroic ratios R of the dissolved dyes. $R = A_\parallel/A_\perp$ means the ratio of the absorbances of light polarized parallel $A_\parallel$ and perpendicular $A_\perp$ to the director $\vec{n}$. The order parameter S is the quantity most commonly used to characterize the mean orientation of the guest molecules. Normally, an optical order parameter

$$S = \frac{A_\parallel - A_\perp}{A_\parallel + 2\,A_\perp} = 1/2\,(3\cos^2\Theta - 1)$$

is calculated, Θ being the angle between $\vec{n}$ and the transition moment fixed by the geometry of the dye molecule. By today's standards, S should be above 0.73. The direction of orientation of the dye molecules has been assumed to be largely determined by their shape[11,12], and, of course, by the order parameter of the host material. It often happens that the degree of order of the guest molecules exceeds that of the host molecules[13]. This has been plausibly explained in terms of the normally greater length of the dye molecules which tend to balance out the more extreme deviations of the smaller host molecules from $\vec{n}$.

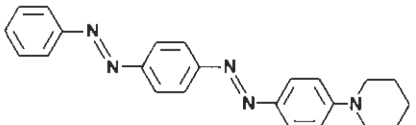
According to the theory of *W. Maier* and *A. Saupe*[14], the dispersion interactions with the host molecules can be regarded as optimum with cylindrical molecules having high length to diameter ratios[15]. The results obtained with mono, bis and tris azo compounds such as **1**[16], **2**[17], and **3**[18] can be interpreted in this way. The order parameters of some anthraquinone dyes as **4**[21] and **5**[22] still seemed to be in accord with this interpretation under the condition that the direction of the longest molecular axis is almost coincident with the direction of the transition moment as well as with $\vec{n}$. However, the difficulty in obtaining an agreement between the order parameter, estimated according to the theory of *W. Maier* and *A. Saupe*, and the measured order parameter of the transition moments for plate-like molecules such as certain anthraquinone compounds has already been pointed out[15]. The order parameters of anthraquinone dyes of types 6 to 8 have recently been determined[23]. A look at the molecular shape must give rise to doubts as to whether preferred cylindrical envelopes can be rationalized in these cases and, in the special case of 8, as to which of the axes through the plane of the anthraquinone system should give preferred dye-host interactions. Recently, some perylene dyes with relatively small ratios of molecular length to width were tested in guest-host displays. The optical order parameters are reported to be very high[24].

The question arises whether other explanations for the order of plate-like molecules can be applied. The mean field lattice model proposed by *P. J. Flory*[25], which is based on *Onsager*'s theory[26] of hard rods, has been applied to mixtures of rod-like and plate-like molecules[27]. Minimizing the excluded volume leads to the assumption of biaxial nematic states, in which the plate-like molecules are oriented parallel to each other. It has been concluded that such mixtures can have elevated transition temperatures between the nematic states and the isotropic states when compared to the original nematic phase[28]. To find out whether there are similar effects with dye molecules, the tris azo dye 3 and an anthraquinone dye of type 6 were dissolved in two hosts of different polarity (Fig. 3). The straight lines obtained for the azo dye are not surprising for a rod-like additive. Clearly, there are no deviations from linearity due to the formation of molecular associations. The behavior of the anthraquinone dye is quite different, showing a feature similar to other plate-like molecules in nematic phases[28]. It can concluded that the planes of the plate-like molecules are parallel to $\vec{n}$ resulting in higher T_{NI} values,



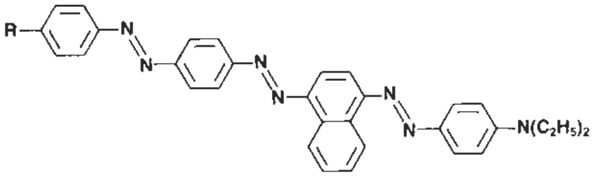
1

S = 0.70 in E 7[19] at 20 °C, blue



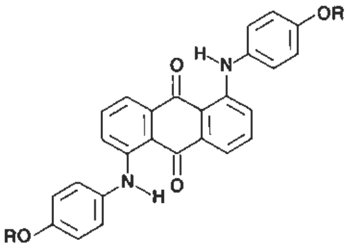
2

S = 0.74 in E 7 at 20 °C, red



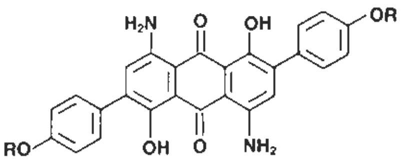
3

R = C_4H_9, S = 0.79 in ZLI 1840[20] at 20 °C, bluish-purple



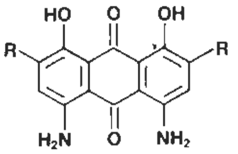
4

R = C_5H_{11}, S = 0.68 in E 7 at 20 °C, violet



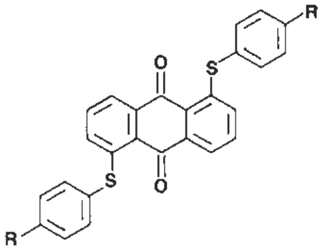
5

R = C_5H_{11}, S = 0.74 in E 7 at 20 °C, blue



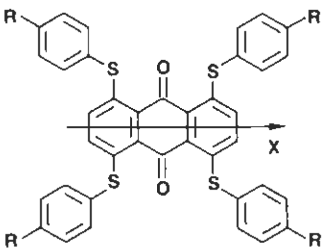
6

R = $i-C_4H_9$, S = 0.73 in E 43[19] at 20 °C, blue



7

R = H, S = 0.79 in E 43 at 20 °C, yellow



8

R = H, S = 0.80 in E 43 at 20 °C, red

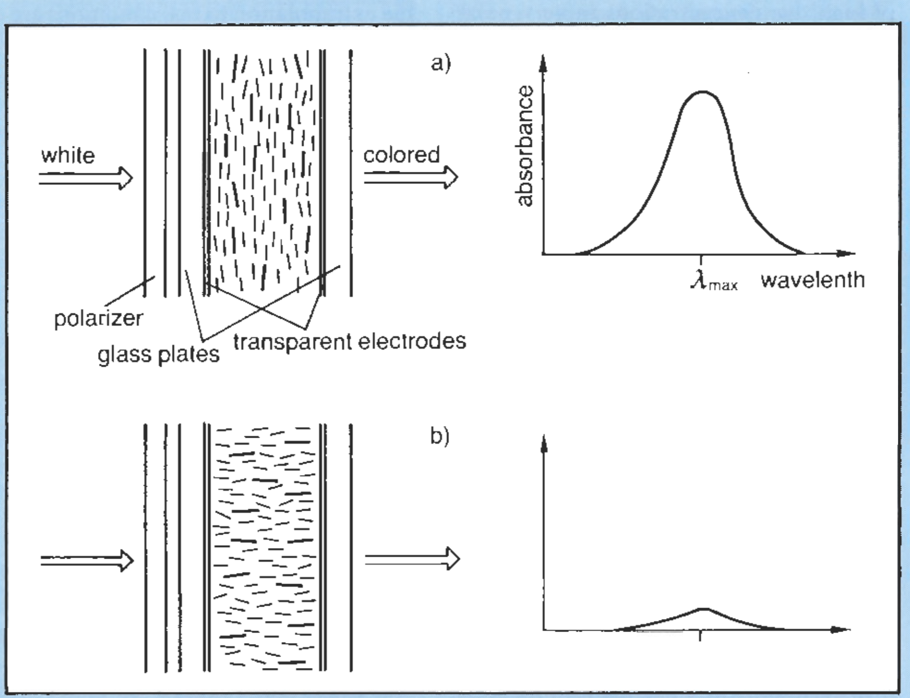
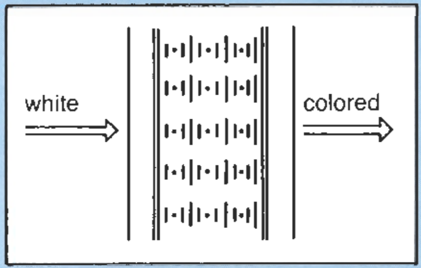


Figure 1: Path of light throug a *Heilmeier* cell.
a) off-state, b) on-state of the electric field.

Figure 2: Planar cholesteric arrangement of dye molecules in a *White-Tayor* cell.



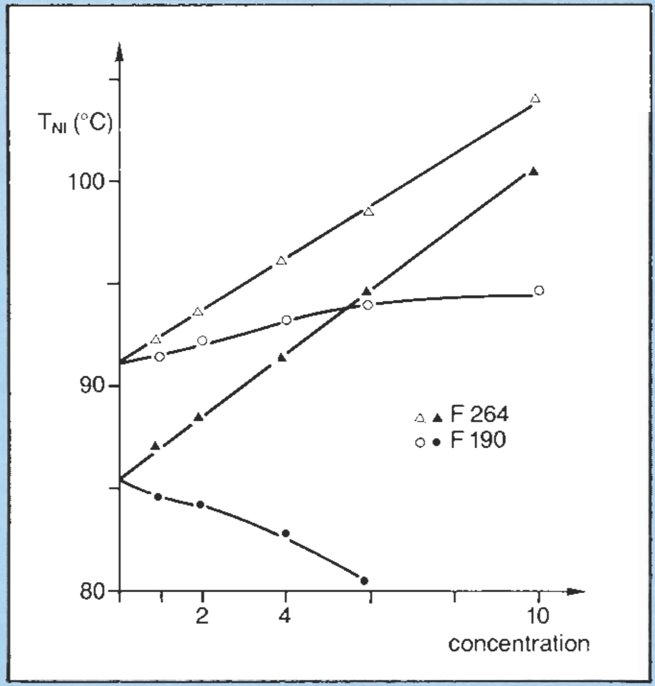


Figure 3: T_{NI} values in °C for solutions of the tris azo dye F 264 (3) and the anthraquinone dye F 190 (6) in ZLI 1840 (open symbols, mean dielectric constant, $\epsilon = 8.0$) and in ZLI 1957/5[20] (solid symbols, $\epsilon = 5.0$) vs. concentration (percentage by mass).

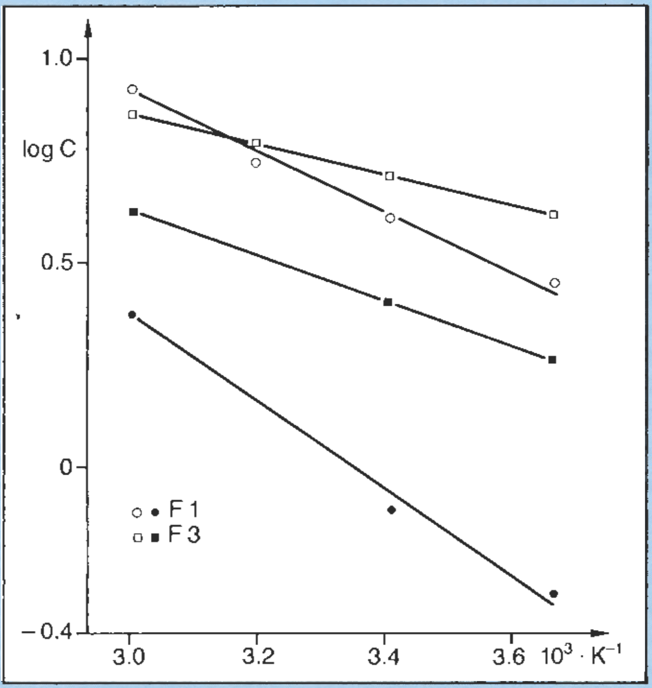


Figure 4: Solubility of the anthraquinone dye F 1 (6) and F 3 (7) in ZLI 1840 (open symbols) and ZLI 1957/5 (solid symbols); common logarithm of concentration (percentage by mass) vs. reciprocal temperature ($10^3 \cdot K^{-1}$).

although it is hard to understand why, at concentrations of the order of one per cent of an anthraquinone dye, the normals to the plates should also be parallel. Quite recently, the energies of interactions between rod-like molecules and anthraquinone dyes have been refined by the additional assumption of dipole-induced dipole forces[29]. As an alternative to the explanations given above, the order of guest molecules in liquid crystalline matrices can be deduced from the variational principle of maximum flux of energy[30].

Absorbance

Having shown that dyes can be made available with a high dichroic ratio, the question has to be put forward as to whether the concentration of the dyes in the nematic solution can be made high enough to obtain a sufficient absorbance for a layer of about 10 µm. The solution to this problem depends on:

i) The solubility of the dyes at the lowest temperature occurring in practice. For multi-dye mixtures, the mutual influence on solubility has to be taken into account.

ii) The molecular absorption coefficient in relation to molecular weight and the width of the absorption curve of a single dye.

iii) Display technique, i.e. whether transmissive of reflective mode is preferred.

Measurements of the solubilities of a variety of dyes in different hosts have been made in the past. Unfortunately, it was often found that the values of the concentrations were not taken from equilibrated solutions. An appropriate method of measuring solubilities at low temperatures has to make sure that a thermodynamically stable system is achieved[31]. Fig. 4 shows typical plots of the solubilities for some anthraquinone dyes in hosts of different polarity. If the dye exists in different crystal modifications, it should be ensured that the least soluble one is examined. Encouraging results with respect to solubility at 20 °C have recently been reported for compounds of type 7 with a *tert.*-butyl substituent[23]. Fig. 4 emphasizes the dependence of solubility on the polarity of the host material. The obvious feasibility of high dye concentrations in very polar hosts, however, is restricted by the higher viscosities of such mixtures increasing the switching time of the displays.

The dependence of the molar absorption coefficients and of the absorption maxima λ_{max} of chromophoric systems on chemical structure can he obtained from general works[32]. Tab. 1 gives a comparison of some dyes which can be used for guest host displays. $A^{1\%}_{1\,cm}$ means the practical absorbanc of a one per cent by mass isotrocpic solution in chloroform with a thickness of 1 cm. In order to obtain a good appearance of a display switching between black and white it is necessary to have a good absorbance over the entire spectrum of visible light. Therefore a broad absorption curve of a single dye, represented by the value $\lambda_{1/2}$ in Tab. 1. is advantageous. Also with regard to the quality of the contrasting black and white which both must be free from colored tinges, the composition of the dyes has to be optimized. This is complicated by the fact that values of R for different dyes are not identical[33].

Dye Code (E. Merck)	Type	$A^{1\%}_{1\,cm}$	λ_{max} [nm]	$\lambda_{1/2}$
F 264	3	882	560	144
F 1	6	605	640	95
F 3	7	216	463	80
F 2	8	240	555	76

Table 1: Practical absorbance $A^{1\%}_{1\,cm}$ in cloroform, absorption maxima (nm) and widths of the absorption curve at half of the maximum value, $\lambda_{1/2}$ (nm), in ZLI 1840[20].

Stability

Whereas the fastness of the dyes discussed for displays technology towards reactions with oxygen, moisture and the liquid crystalline solvent itself can be regarded as sufficient, light-fastness is still the determining factor for the lifetime of guest-host displays. It is difficult to predict the light-fastness of dyes on the basis of their chemical structure. Although there are rough empirical rules, the influence of the matrix on the fate of an excited π-π^* transition state cannot be easely forseen. Therefore, lifetime tests under conditions that permit the extrapolation to real conditions are essential.

Many of the anthraquinone dyes tested[21-23] under visible and U. V. light proved to be sufficiently stable. Although in the past there have been many doubts regarding the applicability of azo dyes in displays encouraging results were obtained with yellow, orange, red and even bluish-purple azo dyes [17, 34]. A U. V. cut filter on the displays was, however, indispensible.

Acknowledgment
This work has been supported by the Bundesministerium für Forschung und Technologie of the Federal Republic of Germany. The author is solely responsible for the content.

References:

1) FREDERIKS, V., TSVETKOV, V.: Acta Physicochim. USSR 3, 879, 895 (1935)
2) SCHIEKEL, M. F., FAHRENSCHON, K.: Appl. Phys. Lett. 19, 391 (1971)
3) SCHADT, M., HELFRICH, W.: Appl. Phys. Lett. 18, 127 (1971)
4) See also ERDMANN, D.: Kontakte (Darmstadt) 1976 (2), 37
5) HEILMEIER, G. H., ZANONI, L. A.: Appl. Phys. Lett. 13, 91 (1968)
6) WHITE, D. L., TAYLOR, G. N.: J. Appl. Phys. 45, 4718 (1974)
7) ALT, P. M., PLESHKO, P.: IEEE Trans. Electron Devices ED-21, 146 (1974)
8) SCHEFFER, T. J.: J. Appl. Phys. 53, 257 (1981)
9) UCHIDA, T., WADA, M.: Mol. Cryst. Liq. Cryst. 63, 19 (1981)
10) EIDENSCHINK, R.: Kontakte (Darmstadt) 1979 (1), 15
11) BAHADUR, B., SARNA, R. K., BHIDE, V. G.: Mol. Cryst. Liq. Cryst. 75, 121 (1981)
12) GRAY, G. W.: Dyes Pigm. 3, 203 (1982)
13) WEDEL, H., HAASE, W.: Ber. Bunsenges. Phys. Chem. 80, 1342 (1976)
14) MAIER, W., SAUPE, A.: Z. Naturforsch. A 14, 882 (1959); ibid, A 15, 287 (1960)
15) OSMAN, M. A., PIETRONERO, L., SCHEFFER, T. J., ZELLER, H. R.: J. Chem. Phys. 74, 5377 (1981)
16) CONSTANT, J., RAYNES, E. P., SHANKS, I. A., COATES, D., GRAY, G. W., McDONNELL, D. G.: J. Phys. D 11, 469 (1978)
17) COGNARD, J., HIEU PHAN, T.: Mol. Cryst. Liq. Cryst. 68, 207 (1980)
18) SEKI, H., SHISHIDO, C., YASUI, S., UCHIDA, T.: Jpn. J. Appl. Phys. 21, 191 (1982)
19) A nematic phase of BDH Chemicals Ltd., Poole, England
20) A nematic phase of E. Merck, Darmstadt, W. Germany
21) PELLAT, M. G., ROE, I. H. C., CONSTANT, J.: Mol. Cryst. Liq. Cryst. 59, 299 (1980)

22) COGNARD, J., HIEU PHAN, T.: Mol. Cryst. Liquid. Cryst. 70, 1 (1981)

23) SAUNDERS, F. C., HARRISON, K. J., RAYNES, E. P., THOMPSON, D. J.: Conf. Rec. Bienn. Display Conf. IEEE, Cherry Hill, October 1982

24) OSMAN, M. A., ZELLER, H. R., MARKERT, J.: European Patent Application 0 047 027

25) FLORY, P. J.: Proc. R. Soc. Lond. A 234, 73 (1956)

26) ONSAGER, L.: N. Y. Acad. Sci. 51, 627 (1949)

27) ALBEN, R.: J. Chem. Phys. 59, 4299 (1973)

28) SIGAUD, G., ACHARD, M. F., HARDOUIN, F., GASPAROUX, H.: Chem. Phys. Lett. 48, 122 (1977)

29) SAUNDERS, F. C., WRIGHT, L., CLARK, M. G.: "Liquid Crystals and Ordered Fluids", Vol. 4 (Ed. *J. F. Johnson* and *A. C. Griffin*), Plenum, New York, in press

30) EIDENSCHINK, R.: Kontakte (Darmstadt) 1980 (3), 12; idem: 9th International Liquid Crystal Conference, Bangalore 1982, Abstract C14. This hypothesis relates the activation and deactivation of vibrational modes to a flux of energy, regardless if these processes occur via radiation or thermal exchange with other modes of vibration, rotation or translation. It is noticed that also in the case of 8 there are many polar vibrational modes having a preferential direction parallel to x.

31) FOITZIK, J. K., HAASE, W.: Mol. Cryst. Liq. Cryst. 82, 131 (1982)

32) GRIFFITH, J.: "Colour and Constitution of Organic Molecules," Academic Press, London 1976

33) SCHEUBLE, B. S., WEBER, G., POHL, L., JUBB, R. E.: "Dig. Tech. Pap. SID 1983, 176, Philadelphia 1983

34) SEKI, H., SHISHIDO, C., UCHIDA, T., WADA, M.: Mol. Cryst. Liq. Cryst. 66, 209 (1981)

Author's address:
Dr. Rudolf Eidenschink
E. Merck, Darmstadt
Forschung Industriechemikalien
D-6100 Darmstadt 1
Postfach 41 19

Licristal®
Flüssige Kristalle MERCK

A. Einzelsubstanzen

13858 Licristal® ZLI 1236 (PCH 2) [*trans*-4-Ethyl-(4-cyanophenyl)-cyclohexan]

11864 Licristal® ZLI 1103 (PCH 3) [*trans*-4-Propyl-(4-cyanophenyl)-cyclohexan]

13859 Licristal® ZLI 1188 (PCH 4) [*trans*-4-Butyl-(4-cyanophenyl)-cyclohexan]

11879 Licristal® ZLI 1114 (PCH 5) [*trans*-4-Pentyl-(4-cyanophenyl)-cyclohexan]

11880 Licristal® ZLI 1115 (PCH 7) [*trans*-4-Heptyl-(4-cyanophenyl)-cyclohexan]

15356 Licristal® ZLI 1484 (PCH 32) [*trans*-4-Propyl-4-ethylphenylcyclohexan]

15407 Licristal® ZLI 1476 (PCH 302) [*trans*-4-Propyl-(4-ethoxyphenyl)-cyclohexan]

15408 Licristal® ZLI 1477 (PCH 304) [*trans*-4-Propyl-(4-butoxyphenyl)-cyclohexan]

11882 Licristal® ZLI 1131 (BCH 5) [4-Cyano-4'-(*trans*-4-pentylcyclohexyl)-biphenyl]

15221 Licristal® ZLI 1409 (BCH 52) [4-Ethyl-4'-(*trans*-4-pentylcyclohexyl)-biphenyl]

15359 Licristal® ZLI 1544 (CBC 53) [4-(*trans*-4-Pentylcyclohexyl)-4'-(*trans*-4-propylcyclohexyl)-biphenyl]

15149 Licristal® ZLI 1222 (HP 33) [4-Propylphenyl-4-(*trans*-4-propylcyclohexyl)-benzoat]

15038 Licristal® ZLI 1223 (HH 53) [*trans*-4-Propylcyclohexyl-4-(*trans*-4-pentylcyclohexyl)-benzoat]

15039 Licristal® ZLI 1224 (HH 33) [*trans*-4-Propylcyclohexyl-4-(*trans*-4-propylcyclohexyl)-benzoat]

15151 Licristal® ZLI 1232 (HH 23) [*trans*-4-Propylcyclohexyl-4-(*trans*-4-ethylcyclohexyl)-benzoat]

15153 Licristal® ZLI 1273 (HH 43) [*trans*-4-Propylcyclohexyl-4-(*trans*-4-butylcyclohexyl)-benzoat]

11649 Licristal® ZLI 811 (DE 608) S-(+)-2-Octyl-[4-(4-hexyloxybenzoyloxy)-benzoat]

Neu:
11715 Licristal® ZLI 245 (P 105) [(4-Pentylphenyl)-4-methoxybenzoat]

Neu:
11716 Licristal® ZLI 1004 (P 605) [(4-Pentylphenyl)-4-hexyloxybenzoat]

15237 Licristal® ZLI 1495 (D 501) [4-Methoxyphenyl-*trans*-4-pentylcyclohexylcarboxylat]

15236 Licristal® ZLI 1496 (D 302) [4-Ethoxyphenyl-*trans*-4-propylcyclohexylcarboxylat]

15235 Licristal® ZLI 1497 (D 55) [4-Pentylphenyl-*trans*-4-pentylcyclohexylcarboxylat]

15238 Licristal® ZLI 1563 (D 402) [4-Ethoxyphenyl-*trans*-4-butylcyclohexylcarboxylat]

16096 Licristal® ZLI 1906 (PDX 3) [*trans*-5-Propyl-2-(4-cyanophenyl)-1,3-dioxan]

16097 Licristal® ZLI 1907 (PDX 4) [*trans*-5-Butyl-2-(4-cyanophenyl)-1,3-dioxan]

16098 Licristal® ZLI 1908 (PDX 5) [*trans*-5-Pentyl-2-(4-cyanophenyl)-1,3-dioxan]

B. Gebrauchsfertige Mischungen für die verdrillte Zelle

11878 Licristal® ZLI 1132 (Nem. Phase)
13786 Licristal® ZLI 1221 (Nem. Phase)
13877 Licristal® ZLI 1289 (Nem. Phase)
15241 Licristal® ZLI 1565 (Nem. Phase)
15342 Licristal® ZLI 1636 (Nem. Phase)
15364 Licristal® ZLI 1694 (Nem. Phase)

Neu:
15582 Licristal® ZLI 1957/5 (Nem. Phase)
16504 Licristal® ZLI 2009 (Nem. Phase)
15744 Licristal® ZLI 2116-000 (Nem. Phase)
15743 Licristal® ZLI 2116-100 (Nem. Phase)
16230 Licristal® ZLI 2140-000 (Nem. Phase)
16231 Licristal® ZLI 2140-100 (Nem. Phase)