



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl18>

The Synthesis and Liquid Crystal Transition Temperatures of a Broad Range of Mesogens Incorporating Four- Unit-Linking Groups I

S. M. Kelly^a

^a F. Hoffmann-La Roche Ltd. Central Research Units, CH-4002, Basel,
Switzerland

Version of record first published: 04 Oct 2006.

To cite this article: S. M. Kelly (1991): The Synthesis and Liquid Crystal Transition Temperatures of a Broad Range of Mesogens Incorporating Four-Unit-Linking Groups I, *Molecular Crystals and Liquid Crystals*, 204:1, 27-35

To link to this article: <http://dx.doi.org/10.1080/00268949108046591>

PLEASE SCROLL DOWN FOR ARTICLE

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

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.

The Synthesis and Liquid Crystal Transition Temperatures of a Broad Range of Mesogens Incorporating Four-Unit-Linking Groups I†

S. M. KELLY

F. Hoffmann-La Roche Ltd, Central Research Units, CH-4002 Basel, Switzerland

(Received July 26, 1991)

The vast majority of liquid crystals synthesized over the last one hundred years contain aromatic and/or aliphatic rings joined together either directly or by a central linking unit.¹ These central linkages have nearly always consisted of two units (e.g., $-\text{COO}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{CH}=\text{CH}-$, $-\text{C}\equiv\text{C}-$, $-\text{CH}=\text{N}-$, $-\text{N}=\text{N}-$, $-\text{N}=\text{N}(\text{O})-$) of which only a few have found wide commercial acceptance for display device applications.² Various investigations^{1–5} of compounds incorporating central linkages with four constituent elements (e.g., $-\text{CH}_2\text{CH}_2\text{COO}-$, $-\text{CH}=\text{CHCOO}-$, $-\text{C}_4\text{H}_8-$) reveal a pronounced tendency for smectic mesophase formation. As yet no compounds suitable for display devices have been prepared. We now report a systematic study of new mesogens incorporating four-unit-linkages which are eminently suitable for electrooptic display device applications (e.g., TN, STN, TFT, ECB, GH, SSFLCD, etc.) exhibiting wide-range enantiotropic smectic and nematic mesophases of positive as well as negative dielectric anisotropy.

Keywords: *liquid crystals, four-unit linking group, synthesis, electrooptic display*

INTRODUCTION

Thermotropic liquid crystals generally consist of two or more aliphatic and/or aromatic rings (e.g., cyclohexane, benzene, etc.) bearing two terminal end-groups (e.g., alkyl, alkoxy, halogen, nitrile) and connected to each other by a single carbon-carbon bond ($-$) or by a central linking group (e.g., $\text{CH}=\text{CH}$, $\text{C}\equiv\text{C}$, $\text{CH}=\text{N}$, $\text{N}=\text{N}$, $\text{N}=\text{N}(\text{O})$, COS , COO , C_2H_4 , CH_2O , etc.) in a more-or-less linear, lathe-like structure.¹ Out of the large number of available molecular building blocks suitable for liquid crystalline structures, only a few have been utilized in limited combinations in commercially useful liquid crystals for electrooptic display applications.² The number of useful linking groups is especially limited due to the inability of most known linkages (e.g., $\text{CH}=\text{CH}$, $\text{CH}=\text{N}$, $\text{N}=\text{N}$, $\text{N}=\text{N}(\text{O})$, COS ,

† Presented at The Thirteenth International Liquid Crystal Conference, Vancouver, British Columbia, Canada, 22–27 July 1990.

etc.) to fully satisfy the requirements (e.g., chemical, thermal, and photo-chemical stability) of electrooptic applications. Even stable linkages (e.g., CH_2O) may find no usage due to a general tendency to induce high melting points and/or viscosity (resulting in solubility problems and long response times). The large majority of commercially useful liquid crystals for the electrooptic display industry contain only three central linkages (i.e., $—$, C_2H_4 and COO), each associated with various advantages and disadvantages, reflected in, for example, ease of preparation, transition temperatures, viscosity behaviour, elastic and dielectric constants, smectic tendencies, etc.²

Attempts to introduce alternative central linking units into the liquid crystal field have concentrated mainly on four-unit-linking systems (i.e., $\text{CH}_2\text{CH}_2\text{COO}$, $\text{CH}=\text{CHCOO}$, and C_4H_8).^{3–5} Central linkages containing an uneven number of linking units (e.g., CH_2 , O , CO) lead to the suppression of liquid crystal tendencies, resulting in very low, mostly monotropic clearing points.⁶ This can be explained in terms of the nonlinear configurations of these structures. Four-unit-linking units can be expected to lead to linear, rod-like conformations, which are not possible for the unevenly linked structures, assuming lower free energy values for a parallel arrangement of the molecules. However, the few substances synthesized so far have exhibited predominantly smectic mesophases at elevated temperatures.^{3–5} Reports of nematic or chiral nematic phases are exceptionally rare and those reported are either extremely narrow-range or strongly monotropic. Additionally the linkages containing an ester unit (i.e., $\text{CH}=\text{CHCO}_2$ and $\text{CH}_2\text{CH}_2\text{CO}_2$) are expected to be of higher viscosity and are known, in one case (i.e., $\text{CH}=\text{CHCO}_2$) to be thermally and photochemically unstable.³ This has led to the prevalent view that four-unit-linking groups are unsuitable for liquid crystal formation in general and for electrooptic display applications in particular.²





The study of alternative central linkages incorporating four-unit-linking groups has now been extended from the butyl linkage (C_4H_8) to include *trans*-3-butenyl (C_4H_6), 3-propyloxy ($\text{C}_3\text{H}_6\text{O}$), and (E)-allyloxy ($\text{C}_3\text{H}_4\text{O}$). All of these four-unit-linking groups have been incorporated in molecular structures, chosen to be of potential interest for commercial, electrooptic applications (e.g., TN, STN, TFT, ECB, GH, SSFLCD, etc.), requiring wide-range enantiotropic smectic and/or nematic mesophases of positive or negative dielectric anisotropy. The synthesis of these new materials has been described in detail elsewhere.⁷

RESULTS

The liquid crystal transition temperatures and some enthalpies of fusion of the ethers (I) that differ only in the number of carbon atoms (m) in the alkoxy chain and in the nature of the central linking unit ($Z = \text{C}_4\text{H}_8$, C_4H_6 , $\text{C}_3\text{H}_6\text{O}$ and $\text{C}_3\text{H}_4\text{O}$) are collated in Table I. The 1-alkoxy-4-[4-*trans*-4-pentylcyclohexyl]-1-butyl-benzenes ($Z = \text{C}_4\text{H}_8$) exhibit short-range, mostly enantiotropic smectic B mesophases at or just above room temperature. The smectic B-isotropic transition temperature rises with increasing chain length ($m = 1 - 6$). No identifiable trends for the melting point (C-S_B and C-I) can be established. The introduction of a

TABLE I

The liquid crystal transition temperatures ($^{\circ}\text{C}$) and some enthalpies of fusion (KJ mol^{-1}) for the compounds (I)

$\text{C}_5\text{H}_{11}-\text{C}_6\text{H}_{10}-\text{Z}-\text{C}_6\text{H}_4-\text{OC}_m\text{H}_{2m+1}$						
m	Z	C-S _B /S _A /N/I	S _B -I	S _A -N/I	N-I	ΔH
1		27	(16)	—	—	23.5
2	"	18	31	—	—	14.6
3	"	39	(28)	—	—	33.3
4	"	29	43	—	—	31.4
5	"	31	39	—	—	27.1
6	"	33	46	—	—	
1		25	—	—	34	17.5
2	"	34	—	—	51	17.9
3	"	32	42	—	—	10.2
4	"	24	53	—	—	12.1
5	"	28	52	—	—	9.9
6	"	32	56	—	—	32.9
1		47	—	—	(46)	32.7
2	"	50	—	—	57	22.6
3	"	51	—	—	(48)	31.7
4	"	59	—	(45)	(55)	40.6
5	"	42	—	48	53	22.2
6	"	44	—	54	57	28.8
7	"	51	—	57	—	42.0
1		44	—	—	46	27.5
2	"	62	—	—	(59)	28.5
3	"	72	—	—	(50)	38.7
4	"	59	—	(43)	61	30.9
5	"	41	—	46	54	17.2
6	"	50	—	55	60	28.4
7	"	42	—	57	58	32.0

trans-carbon-carbon double bond into the butane compounds to form the 1-alkoxy-4-(4-[(*E*)-3-(*trans*-4-pentylcyclohexyl)-1-butenyl])benzenes ($\text{Z} = \text{C}_4\text{H}_6$) results in no change in the melting point (C-S_B and S_B-I), a substantial increase ($+20^{\circ}\text{C}$, on average) in the smectic B-isotropic transition temperature (S_B-I) and the appearance of an enantiotropic nematic mesophase (N-I) for two homologues ($m = 1$ and 2). The replacement of a methylene unit (CH_2) in the butyl linking unit of the compounds (I) by an oxygen atom to yield the 1-alkoxy-4-[3-(*trans*-4-pentylcyclohexyl)-1-propyloxy]benzenes ($\text{Z} = \text{C}_3\text{H}_6\text{O}$) increases the melting point (C-S_B,

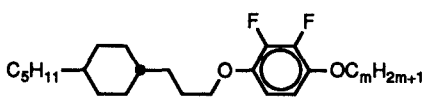
C-S_A, C-N and C-I) significantly (+19°C, on average) comparing only those homologues of similar chain length. The smectic B mesophase is replaced by a smectic A mesophase at higher temperatures (+18°C, on average) and a nematic mesophase is observed for most of the series at relatively elevated temperatures (53°C, on average). The presence of an additional *trans*-carbon-carbon double bond in the 1-alkoxy-4-[(E)-3-(*trans*-4-pentylcyclohexyl)allyloxy]benzenes (Z = C₃H₄O) causes only marginal increases (+5°C and +2°C, on average, respectively) in the melting point (C-S_A, C-N and C-I) and the clearing point (S_A-I and N-I), whereas the smectic A mesophase remains unchanged (on average).

The enthalpies of fusion (ΔH) of all four series of ethers (I) exhibit moderate values in general and in several cases low values, which can be attributed to crystal-smectic transitions (C-S_B and C-S_A).

The liquid crystal transition temperatures and enthalpies of fusion of the 1-n-alkoxy-2,3-difluoro-4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzenes (II) ($m = 1 - 7$) are collated in Table II. The melting point (C-S_A and C-N) decreases with increasing chain length from being significantly above room temperature (C-N = 44°C) for the shortest chain length possible ($m = 1$) to substantially below room temperature (C-S_A = 8°C) for the longest chain length studied ($m = 7$). Melting points at or just below room temperature are observed for intermediate chain lengths ($m = 2 - 6$). The usual pattern of alternation is observed. An enantiotropic smectic mesophase (S_A) is observed below room temperature for the longest chain length studied. The consequence of these trends for the melting point (23°C, on average) and the clearing point (25°C, on average) is a narrow-range, enantiotropic nematic mesophase (2°C, on average) for most of the homologues prepared. However, reasonably wide-range nematic phases (8°C–14°C) are exhibited by several homologues ($m = 6$ and 7) with long terminal alkoxy-chains. The enthalpies of fusion (ΔH) of the ethers (II) are of a normal magnitude (28.6 KJ mol⁻¹, on average) for nematic materials. These compounds of negative dielectric anisotropy

TABLE II

The liquid crystal transition temperatures (°C) and some enthalpies of fusion (KJ mol⁻¹) for the compounds (II)



m	C-S _A /N/I	S _A -N	N-I	ΔH
1	44	—	(26)	30.2
2	25	—	26	25.4
3	21	—	(19)	30.1
4	20	—	22	34.6
5	20	—	22	20.3
6	20	—	28	30.9
7	8	14	28	

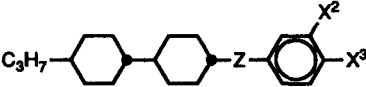




are useful for electrooptic displays based on electrically controlled birefringence (e.g., ECB).¹⁵

The liquid crystal transition temperatures and some enthalpies of fusion for the three-ring materials (III) containing the four-unit-linking groups under investigation, (E)-3-butenyl, butyl, (E)-allyloxy, and propyloxy ($Z = C_4H_6$, C_4H_8 , C_3H_4O , and C_3H_6O , respectively) and one or two substituents (X^2 , $X^3 = H$, F and/or OCF_3) are collated in Table III. The butyl compounds ($Z = C_4H_8$) exhibit a low melting point (34°C, on average), an enantiotropic smectic B-nematic phase transition (69°C, on average) and a relatively high clearing point (127°C, on average). The incorporation of a *trans*-carbon-carbon bond in the butyl compounds to yield the butylene compounds results in an increase (+29°C) in the nematic temperature range by decreasing both the melting point (−13°C, on average) and the smectic B-nematic phase transition temperature (−12°C), while, at the same time, increasing the clearing point (+17°C).

The introduction of an oxygen atom in the butyl materials to give, the propyloxy substances ($Z = C_3H_6O$) increases both the melting and clearing points (+20°C and +16°C, on average, respectively) while decreasing the smectic B-nematic transition temperature significantly, so that only one homologue ($X^2 = H$; $X^3 = OCF_3$) exhibits a smectic B mesophase. The consequence of these changes is an increase in the nematic temperature range (+20°C, on average) due to the suppression of the enantiotropic smectic B mesophase. The incorporation of a *trans*-carbon-carbon double bond in the propyloxy compounds to yield the (E)-allyloxy materials ($Z =$

TABLE III

The liquid crystal transition temperatures (°C) and some enthalpies of fusion (KJ mol^{−1}) for the compounds (III)




						
Z	X ²	X ³	C-S _B /N	S _B -N	N-I	ΔH
	H	F	56	87	116	29.6
"	F	F	39	69	103	30.5
"	H	OCF ₃	47	86	111	27.2
	H	F	33	74	135	27.9
"	F	F	27	50	119	20.4
"	H	OCF ₃	41	83	128	3.1
	H	F	78	—	124	35.8
"	F	F	79	—	107	35.1
"	H	OCF ₃	44	62	117	25.5
	H	F	75	—	127	29.9
"	F	F	48	—	101	27.0
"	H	OCF ₃	43	—	120	

C_3H_4O) results in a melting point decrease (-12°C , on average), the disappearance of the smectic B phase, while the clearing point remains unchanged (116°C , on average). Thus the nematic temperature range is increased further ($+12^\circ\text{C}$, on average). Therefore the allyloxy compounds exhibit the widest nematic temperature range of all four series investigated. These materials of moderately low positive dielectric anisotropy are of interest for directly addressed displays (e.g., TFT).¹⁵

The liquid crystal transition temperatures and some enthalpies of fusion of the 5-n-alkyl-2-substituted phenylpyrimidines (IV) are recorded in Table IV. The melting points (C- S_C and C-N) of all three homologous series of butyl, 3-propyloxy, (E)-3-allyloxy derivatives are very similar (74°C , 79°C , and 81°C , on average, respectively). The butyl compounds ($Z = C_4H_8$) exhibit smectic polymorphism (S_3 , as yet unidentified, S_C and S_A) at elevated temperatures, while the 3-propyloxy and (E)-3-allyloxy materials ($Z = C_3H_6O$ and C_3H_4O) possess are smectic mesophase (S_A). However, the butyl derivatives exhibit a smectic C mesophase and clearing point (N-I) at lower temperatures (77°C and 113°C , on average, respectively) than the corresponding 3-propyloxy (100°C and 135°C , on average, respec-

TABLE IV

The liquid crystal transition temperatures ($^\circ\text{C}$) and some enthalpies of fusion (KJ mol^{-1}) for the compounds (IV)

$C_nH_{2n+1}-\text{C}_5\text{H}_4\text{N}_2-\text{C}_6\text{H}_4-Z-\text{C}_6\text{H}_{11}$							
n	Z	C- S_C /N	S_3 - S_C	S_C - S_A	S_A -N	N-I	ΔH
5		78	—	—	—	119	—
6	"	79	—	—	—	113	18.9
7	"	77	—	—	—	116	18.6
8	"	69	—	(64)	—	110	15.5
9	"	74	(62)	82	97	113	15.9
10	"	66	71	86	102	109	—
5		82	—	—	—	139	19.2
6	"	74	—	—	—	135	—
7	"	84	—	—	—	137	16.1
8	"	79	—	88	—	133	25.3
9	"	83	—	103	—	133	—
10	"	69	—	110	—	130	32.2
5		77	—	—	—	144	—
6	"	83	—	—	—	139	18.1
7	"	91	—	—	—	141	18.5
8	"	87	—	88	—	138	17.2
9	"	79	—	102	—	138	—
10	"	68	—	110	—	134	—

tively) or (E)-3-allyloxy (100°C and 139°C, on average, respectively) materials. Some of these new materials are of direct interest for ferroelectric displays (e.g., SSFLCD).¹⁶

DISCUSSION

The liquid crystal transition temperatures of a series of two-ring alkyl/alkoxy substituted materials differing only in the nature of the central linkage (*Z*) are collated in Table V. The most striking feature of the thermal data in the table is their similarity. The melting points (C-S_B, C-N, and C-I) and the clearing points (S_B-I and N-I) of the compounds incorporating standard linking units (*Z* = C₂H₄, CH₂O, —, and COO) have almost the same average values (39°C and 38°C, respectively) as those of the corresponding materials containing the new four-unit-linking units (*Z* = C₄H₈, C₄H₆, C₃H₆O, and C₃H₄O) on average (36°C and 35°C, respectively). The nematic temperature range of the butenyl compound (*Z* = C₄H₆) is even wider (9°C) than that (4°C) of the ethyl substance, due to its lower melting point (25°C) and identical clearing point (34°C). Both the new materials incorporating oxygen atoms in their linking units (*Z* = C₃H₆O and C₃H₄O) exhibit higher clearing points (both 46°C) than that (38°C) of the corresponding methyleneoxy compound.

The liquid crystal transition temperatures of a similar series of materials incorporating the same linking units, but also an additional *trans*-1,4-disubstituted cyclohexane ring are collated in Table VI. Although the melting point (C-S₂ and C-S_B) of the compounds containing the standard linkages (*Z* = C₂H₄, CH₂O, —, and COO) have almost the same average values (39°C and 38°C, respectively) as those of the corresponding materials containing the new four-unit-linking units (*Z* = C₄H₈, C₄H₆, C₃H₆O, and C₃H₄O) on average (36°C and 35°C, respectively).

TABLE V

The liquid crystal transition temperatures (°C) of the compounds of the structure below differing only in the nature of the central linking unit *Z*








$\text{C}_8\text{H}_{11}-\text{Cyclohexyl}-\text{Z}-\text{C}_6\text{H}_4-\text{OCH}_3$				
<i>Z</i>	C-S _B /N/I	S _B -I	N-I	Reference
	30	—	34	8
	46	—	(38)	9
—	45	—	(15)	10
	36	—	64	11
	27	(16)	—	
	25	—	34	
	47	—	(46)	
	44	—	46	

TABLE VI

The liquid crystal transition temperatures ($^{\circ}\text{C}$) of the compounds of the structure below differing only in the nature of the central linking unit Z

Z	C-S ₂ /S _B	S ₂ -S _B	S _B -N/I	N-I	Reference
	23	—	135	136	12
	70	—	133	143	
	50	—	196	—	13
	70	—	90	156	14
	50	—	111	—	
	67		113	127	
	56	109	113	136	

and COO) is lower (-5°C) and the clearing point (N-I) is higher ($+13^{\circ}\text{C}$) than those of the corresponding substances containing the new linking units ($\text{Z} = \text{C}_4\text{H}_8$, $\text{C}_3\text{H}_6\text{O}$, and $\text{C}_3\text{H}_4\text{O}$), the nematic temperature range (6°C) is not so wide as that ($+20^{\circ}\text{C}$) of the latter materials because of the higher ($+27^{\circ}\text{C}$) smectic-nematic/isotropic transition temperature (S_B -N and S_B -I).

It is probable that the carbon-carbon bonds in the butyl central linkage ($\text{Z} = \text{C}_4\text{H}_8$) prefer to adopt an antiperiplanar, gauche-gauche conformation, thus minimizing intra- and intermolecular interactions, thereby achieving an energy minimum and a high molecular packing density. Thus, introduction of the butyl linkage into a directly bonded molecule results in a substantial increase in the length/breadth ratio of the molecule, without decreasing its linearity of form. This should lead to an increase, or at least a minimal change, in the clearing point which is, indeed, observed to be the case (see Table V), depending upon the proportion of non-linear conformers the butyl linkage adopts at these temperatures. It may be postulated that at higher transition temperatures, as for example in the case of three-ring systems, the proportion of non-linear conformers of the butyl linkage, which are not possible for the directly linked analogue, must be higher. Therefore, the clearing point of the butyl compound may well be lower than that of the corresponding directly bonded compound, which again is seen to be the case (see Table VI). The introduction then of a *trans*-carbon-carbon double bond into the butyl linkage (C_4H_8) to create the butenyl linkage (C_4H_6) must result in an increase in rigidity and a subsequent decrease in the number of possible and probable non-linear conformations. Thus the clearing point should be higher for the butenyl material (as shown in the Tables V and VI) independent of temperature. A similar relationship is observed for the corresponding materials incorporating the propyloxy and allyloxy central linkages ($\text{C}_3\text{H}_6\text{O}$ and $\text{C}_3\text{H}_4\text{O}$, respectively), although at higher

temperatures due to the presence of the highly polarizable oxygen atom in conjugation with the aromatic benzene ring. Thus the two-ring materials incorporating the propyloxy and allyloxy linkages exhibit higher clearing points than the corresponding methyleneoxy compound ($Z = \text{CH}_2\text{O}$), see Table V, whereas for three-ring systems the reverse is the case, see Table VI. The fact that the clearing points of the two-ring and three-ring ester derivatives ($Z = \text{COO}$) are higher than those of any of the corresponding materials discussed above containing the four-unit-linking groups, may be attributable to the rigid, highly polarizable nature of the ester linking, thus allowing a high degree of electron delocalization and conjugation with the aromatic ring. All of these trends have been observed for a much larger and more varied number of new liquid crystal types containing the new four-unit-linking groups described in detail elsewhere.⁷

CONCLUSIONS

The effect of four-unit-linking groups (i.e., butyl, (E)-3-butenyl, 3-propyloxy, and (E)-allyloxy) on the liquid crystal transition temperatures of a wide range of compounds designed with electrooptic display applications in mind has been investigated systematically. A wide variety of novel mesogens possessing wide-range enantiotropic smectic and nematic mesophases of positive as well as negative dielectric anisotropy has been prepared. The two-ring materials generally exhibit clearing points above those of the corresponding compounds containing standard linking units (i.e., C_2H_4 , CH_2O , —, and COO). The reverse is true for analogous three-ring systems. This may be attributable to higher concentrations of non-linear conformations of the four-unit-linking groups at elevated temperatures.

References

1. "Fluessige Kristalle in Tabellen II", eds. D. Demus and H. Zashcke, VEB Deutscher Verlag für die Grundstoffindustrie, Leipzig 1984.
2. E. Poetsch, *Kontakte*, **2**, 15 (1988).
3. T. M. Leslie, *Ferroelectrics*, **58**, 9 (1984).
4. K. Pilorz and H.-J. Deutscher, presented at the Eighth Liquid Crystal Conference of Socialist Countries, Crakow, Poland, 1989.
5. G. W. Gray, D. Holmes, X'-jun Hong, D. Lacey, R. M. Scowston and K. J. Toyne, presented at the Twelfth International Liquid Crystal Conference, Freiburg, FRG, 1988.
6. H.-J. Deutscher, R. Frach and R. Kreig, *18 Freiburger Arbeitstagung fuer Fluessigkristalle*, 1986.
7. S. M. Kelly, *Liquid Crystals*, in press.
8. R. Rich, A. Villiger and E. Widmer, *German Patent Application*, DE-3 201 721 (1981).
9. N. Carr and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **124**, 27 (1985).
10. R. Eidenschink, M. Roemer and F. V. Allen, in "Liquid Crystals and Ordered Fluids," eds. A. C. Griffin and J. F. Johnson, Plenum Press, New York, 1984, p. 737.
11. H.-J. Deutscher, B. Laaser, W. Doelling and H. Schubert, *J. prakt. Chem.*, **320**, 191 (1978).
12. H. Takatsu, K. Takeuchi and H. Sato, *Japan Display*, **83**, 228 (1983).
13. M. Osman, *Mol. Cryst. Liq. Cryst.*, **128**, 45 (1985).
14. R. Eidenschink, *Kontakte*, **1**, 15 (1979).
15. M. Schadt, private communication.
16. S. M. Kelly, J. Fuenfschilling and F. Leenhouts, *Liquid Crystals*, in press.