Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Cycloalka(alke) Nones as Structural Fragments in Liquid Crystals

Vladimir F. Petrov [a]

[a] LC Works, Camberwell, Vic., Australia

Version of record first published: 31 Aug 2006

To cite this article: Vladimir F. Petrov (2005): Cycloalka(alke) Nones as Structural Fragments in Liquid Crystals, Molecular Crystals and Liquid Crystals, 432:1, 15-27

To link to this article: http://dx.doi.org/10.1080/154214090892771

Mol. Cryst. Liq. Cryst., Vol. 432, pp. 15–27, 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214090892771

Taylor & Francis
Taylor & Francis Group

Cycloalka(alke) Nones as Structural Fragments in Liquid Crystals

Vladimir F. Petrov
LC Works, Camberwell, Vic., Australia

The effect on the physicochemical and electrooptical properties of introducing cycloalkanones and cycloalkenones into the molecular structure of liquid crystals is discussed and rationalized in terms of existent theories.

Keywords: cycloalkanones; cycloalkenones; liquid crystals; physicochemical properties

INTRODUCTION

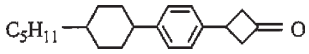
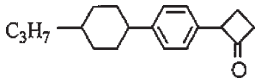
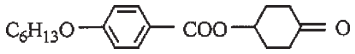
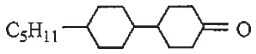
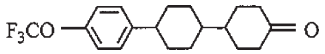
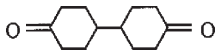
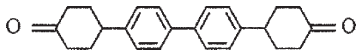
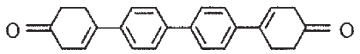
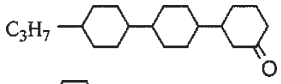
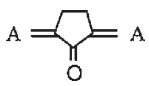
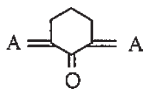
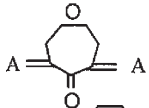
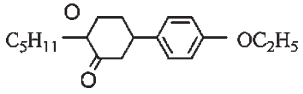
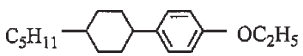
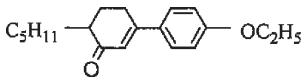
This review focuses on the effect of introducing the fragments containing the exocyclic keto bond into the molecular structure of liquid crystals on their physicochemical and electrooptical properties. It is believed that many characteristic effects of the exocyclic ketonization can be correlated with the geometric and electronic structures of the keto groups [1] and their quantity and positions in the molecule. The pronounced ability of the keto groups to form the hydrogen bonds [2–6] and cause the mesomeric effect, which is due to the conjugation of the keto group with another double bond or with a lone pair of electrons [1], should affect the physicochemical properties of liquid crystals containing cycloalkanones and cycloalkenones.

MESOMORPHIC PROPERTIES

The phase transition temperatures of some ketones and reference compounds are presented in Tables I–IV where Cr, Sm, SmC, SmA, N, and I denote the crystalline, smectic, smectic C, smectic A, nematic, and isotropic phases, respectively.

Address correspondence to Vladimir F. Petrov, LC Works, 6/68 Brinsley Road, Camberwell, Vic. 3124, Australia. E-mail: lcworks@hotmail.com

TABLE I Physicochemical Properties of Some Liquid Crystals

No.	Compound	Phase transitions, °C	Δε	Δn	Reference
1-1		Cr 42 I	2.85[a]	0.071[a]	17
1-2		Cr 44 I	–1.98[b]	0.040[b]	18
1-3		Cr 44 I			19
1-4		Cr 31 I			20
1-5		Cr 74 I			21
1-6		Cr 116 I			22
1-7		Cr 221 I			23
1-8		Cr 238 I			23
1-9		Cr 66 Sm 151 I			24
1-10[c]		Cr 153 SmA 174 N 176 I			25
1-11[c]		Cr 117 N 141 I			25
1-12[c]		Cr 92 N 104 I			25
1-13		Cr 44 I			26
1-14[c]		Cr 51 N (49) I			27
1-15		Cr 70 SmA 86 I			28

[a,b]Extrapolated from 10 wt % solution at 20°C in ZLI-4792 and ZLI-2857, respectively.

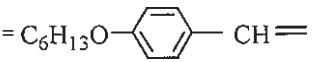
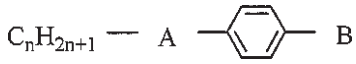
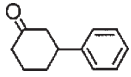
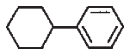
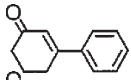
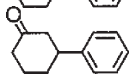
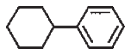
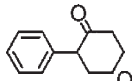
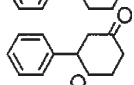
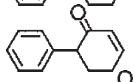
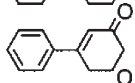
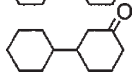
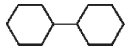
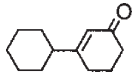
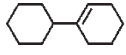
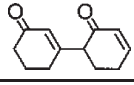
[c]A = 

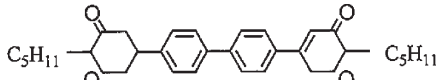
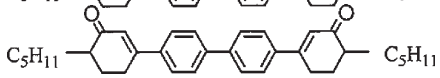
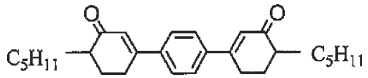
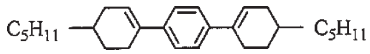
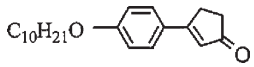
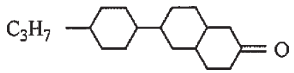
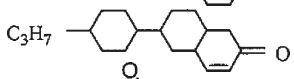
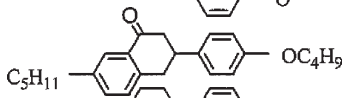
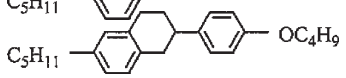
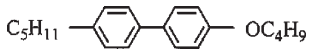
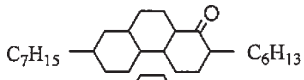
TABLE II Mesomorphic Properties of Liquid Crystals:



No.	n	A	B	Phase transitions, °C	Reference
2-1	5		OC_2H_5	Cr 79 N (76) I	29
2-2	5		CH_3	Cr 84 SmA 148 N 152 I	26
2-3	5		CH_3	Cr 98 Sm 123 N 178 I	30
2-4	5		CH_3	Cr 117 SmA 179 I	28
2-5	5		OCH_3	Cr 112 N 178 I	26
2-6	5		OCH_3	Cr 80 N 165 I	31
2-7	5		OCH_3	Cr 101 N 112 I	32
2-8	5		OCH_3	Cr 127 I	32
2-9	5		OCH_3	Cr 67 N 99 I	32
2-10	5		OCH_3	Cr 63 N 75 I	32
2-11	3		F	Cr 107 N 122 I	32
2-12	3		F	Cr 54.1 Sm 96.6 N 155.2 I	33
2-13	3		F	Cr 105 I	32
2-14	3		F	Cr 45 N 91 I	34
2-15	5		OC_2H_5	Cr 92 SmA 130 N 154 I	28

It has been demonstrated that the cyclobutanone is floppy molecule (compare with puckered, nonplanar parent cyclobutane) [7]. Its slightly distorted chair conformation is a little bit higher in energy than the parent system [8,9].

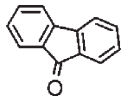
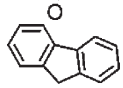
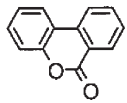
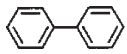
TABLE III Mesomorphic Properties of Some Liquid Crystals

No.	Compound	Phase transitions, °C	Reference
3-1		Cr 118 SmA 225 I	35
3-2		Cr 180 SmA 254 N 275 I	28
3-3		Cr 109 SmA 164 I	28
3-4		Cr 91 Sm 144 N 167 I	36
3-5		Cr 59 I	43
3-6		Cr 59.9 Sm (33) I	50
3-7		Cr 70.8 I	50
3-8		Cr 61 N (37) I	53
3-9		Cr 54.8 N (48.2) I	53
3-10		Cr 37 Sm 80.1 Sm 88.1 I	54
3-11		Cr 93 N 99.5 I	55
3-12		Cr_2 56.5 Cr_1 64.5 N 84 I	55

According to Tamagawa and Hilderbrandt [10], slightly distorted cyclopentanone can either be twisted, with C_2 symmetry, or it can be bent, with C_s symmetry. The twisted and bent ring conformations have the identical energy, which is why the barrier to pseudorotation is equal to zero. Indeed, the pseudorotational motion of substituted cyclopentanones can be more restricted because the energies of the twisted and bent conformers are no longer identical. The stability of these conformers depends on the torsional barriers of the carbon–carbon bond and the bonds involving the substituted atom [10].

On the potential energy surface of cyclohexanone, these are two minima, the chair and twist-boat [11]. The twist-boat is distorted toward the boat conformation. The calculated energy difference

TABLE IV Mesomorphic Properties of Liquid Crystals: $C_8H_{17}O—A—OC_8H_{17}$

No.	A	Phase transitions, °C	Reference
4-1		Cr 55 SmC 85 I	60
4-2		Cr 111 SmA 116.5 I	60
4-3		Cr 80 SmC 99 I	61
4-4		Cr 117.5 I	62

between these two conformations is 3.4 kcal/mol [11]. In cyclohexane there are two types of minima, the chair and twist-boat, and two first-order transition states: the half-chair and boat [11]. The half-chair and twist-boat are calculated to be 8.6 and 5.6 kcal/mol above the chair, respectively. This reveals that the introduction of the carbonyl bond into the cyclohexane significantly lowers the energy difference between the chair and twist-boat conformations. The boat state of the cyclohexane is 1.1 kcal/mol above the twist-boat, whereas the barrier to conversion in the chair is 10.4 kcal/mol [11]. According to Abraham *et al*. [12], the cyclohexanone ring is somewhat flatter at the carbonyl end than cyclohexane, the angle of pucker being reduced from 51° to 49°; that is, the dihedral angle is reduced from 56° to 51°.

It has been shown that the ratio of the total puckering of the twist-chair forms of the cycloheptanone (which exists as a nonrigid pseudo-rotating molecule [13]) and cycloheptane is similar to that of the cyclohexanone and cyclohexane, suggesting that the carbonyl group has the same flattening effect in the cycloheptane and cyclohexane [14]. In the meantime, the carbonyl bond angle, which is one of the important geometrical parameters of the cycloalkanones, increases with their sizes [10,15,16]: cyclobutanone: 92.8°, cyclopentanone: 112.4°, cyclohexanone: 115.3°, cycloheptanone: 117.2°.

One can expect that these structural features of cycloalkanones affect the mesomorphic properties of the liquid crystals incorporating them. Usually, monosubstituted cycloalkanones are not mesomorphic (compounds **1-1**–**1-7**, Table I). Changing the position of the carbonyl bond in cyclohexanones (compound **1-9**, Table I) and/or disubstitution of the cyloalkanone derivatives may introduce the mesophases there

(compounds **1-9**–**1-12**, **2-2**, **2-5**, **2-7**, **2-11**, **3-1**, Tables I–III). As is evident from Table I, the introduction of cyclopentanone, cyclohexanone, and cycloheptanone into the molecular structure of the corresponding 2,5-, 2,6-, and 2,7-bis(4-alkoxy benzylideno) derivatives lowers their clearing (nematic–isotropic or smectic–isotropic phase-transition temperature) and melting (crystal–smectic or crystal–nematic phase-transition temperature) points with increasing the size of cycloalkanones (compounds **1-10**–**1-12**). It reveals that the whole cycloalkanone fragments work as lateral substituents, which increase the molecular width and reduce the intermolecular interactions [37]. In the case of disubstituted trans-cyclohexanones, it can be proposed that only their carbonyl bonds work as lateral substituents, lowering (compounds **1-13**, **1-14**, **2-2**, **2-3**, **2-11**, and **2-12**) and enhancing (compounds **2-5** and **2-6**) the clearing temperatures in comparison with those of the corresponding parent trans-1,4-cyclohexylene derivatives. The decreased clearing points of the cyclohexanone derivatives do not support the theory of Maier and Saupe that increasing the anisotropy of polarizability should enhances the nematic thermostability [38]. In this case, the cyclohexanone derivatives, which have larger polarizability than the corresponding cyclohexane derivatives [39,40], should always exhibit higher clearing temperatures. The melting temperatures of the cyclohexanone derivatives can be lower (compounds **1-13**, **1-14**, **2-2**, and **2-3**) and higher (compounds **2-5**, **2-6**, **2-11**, and **2-12**) in respect to those of the corresponding trans-1,4-cyclohexylene derivatives. As is evident from Table II, the direction of the carbonyl group of cyclohexanone introduced into the molecular core of liquid crystals significantly affects their mesomorphic properties. So far, pointing the carbonyl group of the central cyclohexanone toward the terminal methoxy group of three-ring pentyl-methoxy derivatives results in disappearing the mesophases and increasing the melting temperature (compound **2-8**), whereas the opposite leads to the creation of the narrow nematic phase with moderate thermostability (compound **2-7**).

According to Chadwick *et al*. [41], the equilibrium structure of cyclopent-2-en-1-one has the heavy atoms coplanar in contrast to the puckered structure of cyclopentanone. Significant conjugation is retained in cyclopent-2-enone after the $n \rightarrow \pi^*$ transition to keep the carbonyl oxygen in the plane of the ring [42]. The introduction of cyclopent-2-en-1-one into the molecular structure of two-ring derivatives does not create the mesophases (compound **3-5**, Table III), and the corresponding three-ring derivative exhibits very narrow nematic phase with low thermostability [43].

It has been demonstrated by Abraham and Lucas [44] that in cyclohex-2-en-1-one the envelope conformation is more stable

(ca. 0.5–1.0 kcal/mol) than the half-chair form. Basically, it is a planar ring with the exception of C(5) conjugated with the C=C and C=O bonds and which extends out of the molecular plane [45]. The most probable motion of this molecule is the inversion of C(5) through the molecular plane [46]. The parent cyclohexene is nonplanar with a half-chair (twisted) conformation C_2 [47]. The cyclohexene ring can interconvert from one twisted from to another via the boat (bent) conformation with C_s symmetry. The barrier to interconversion lies in the range 8.4–12.1 kcal/mol [47], whereas the barrier to planarity (energy difference between the planar form C_{2v} and the twisted form) is 13.4 ± 1.4 kcal/mol [47]. Another important thing is the interaction between the methylene hydrogens. For the C_2 form, the C(4) C(5) dihedral angle is 56.6° and C(5) C(6) dihedral angle is 40.9° [48]. For the C_s form, the corresponding angles are 8.7 and 0°, and for the planar form, all the methylene hydrogens are eclipsed [48]. Some examples of using cyclohex-2-en-1-one and the corresponding cyclohexene ring as structural fragments of liquid crystals are presented in Tables I–III. As in the case of cyclohexanones, we can consider the carbonyl bond of cyclohex-2-en-1-one as a lateral substituent, which increases the clearing points (compounds **1-15** and **2-1**, Tables I, II) and results in the disappearance of the mesophases (compounds **2-13** and **2-14**) in respect to those of the corresponding cyclohexene derivatives. The melting temperatures of the cyclohex-2-en-1-one derivatives can be lower (compounds **1-15** and **2-1**) and higher (compounds **2-13** and **2-14**). As is evident from Tables I and II, the clearing temperatures of the cyclohex-2-en-1-one derivatives can be higher (compounds **1-13**, **1-15**, **2-2**, **2-4**, **2-8**, and **2-10**) and lower (compounds **2-7**, **2-9**, **2-11**, and **2-13**) in respect to those of the corresponding cyclohexanone derivatives. Similarly, the melting temperatures can be higher (compounds **1-13**, **1-15**, **2-2**, and **2-4**) and lower (compounds **2-7**, **2-8**, **2-9**, **2-10**, **2-11**, and **2-13**). As in the case of the cyclohexanones, the direction of the carbonyl bond of cyclohex-2-en-1-one significantly affects the mesomorphic properties of three-ring pentyl-methoxy derivatives incorporating this fragment, with higher melting and clearing temperatures recorded for compound having the carbonyl bond pointed toward the pentyl group (compounds **2-9** and **2-10**, Table II). As expected, the introduction of the second cyclohex-2-en-1-one ring into the molecular structure of liquid crystals increases the melting and clearing temperatures (compounds **1-15** and **2-15**, Tables I, II). Compounds **3-2** and **3-3** (Table III) present the other examples of liquid crystals having two cyclohex-2-en-1-one rings that exhibit sufficiently higher melting temperatures than the corresponding cyclohexanone-cyclohex-2-en-1-one and dicyclohexene derivatives (compounds **3-1**,

3-4, Table III), whereas the clearing points can be higher (compounds **3-1** and **3-2**) and lower (compounds **3-3** and **3-4**) in respect to those of the corresponding cyclohexanone-cyclohex-2-en-1-one and dicyclohexene derivatives, respectively.

The fusion of the cyclohexane and cyclohexanone rings results in the formation of 2-decalone fragment. It has been reported by Abraham *et al*. [49] that trans-2-decalone exists as a rigid chair–chair structure. In the gas phase its two rings are distorted chairs with the torsional angle about C(1)–C(2) bond equal to 55.3°. The angle of pucker of the ketone ring in trans-2-decalone in about 51°, similar to that of cyclohexanone, but different from that defined for substituted decalones in solid state, in which significant flattening of the rings happens. Cis-2-decalone has two conformations: steroidal form with three gauche butane interactions and a more stable (ca. 0.8 kcal/mol) nonsteroidal form in which one of these gauche interactions is replaced by a 3-alkyl ketone interactions that have a stabilizing effect. As can be seen from Table III, the introduction of trans-2-decalone into the molecular structure of two-fragment derivative results in the creation of monotropic smectic phase (compound **3-6**), and the corresponding unsaturated ketone **3-7** exhibits no mesophases.

It has been shown that in 1-tetralone, which is a result of the fusion of the benzene and cyclohexanone rings, the envelope conformation is more stable (ca. 0.94 kcal/mol) that the half-chair conformation [51]. In the corresponding parent tetraline the saturated ring exists in a half-chair form similar to cyclohexene. The introduced methyl group at C(1) position of tetraline preferentially orients pseudoaxially, whereas a methyl group at C(2) prefers the equatorial position [52]. As is evident from Table III, two-fragment derivative **3-8** with 1-tetralone shows monotropic nematic phase with a significantly lower clearing temperature and higher melting point in comparison with that of the corresponding tetraline (compound **3-9**) and biphenyl (compound **3-10**) derivatives.

Similar trends can be observed in Table III for perhydro-phenanthren-1-one derivative **3-11** and the corresponding perhydro-phenanthrene derivative **3-12**, with higher melting and nematic–isotropic phase transition temperatures observed for the former compound.

It has been demonstrated that the crystalline fluoren-9-one is planar where benzene rings are fused to cyclopentanone [56,57]. This fusion reduces the angels at the fusion points at the C(1) and C(4) positions below 120°, which is 118° [56]. As is evident from Table IV, dioctyloxy substitution of planar and rigid fluoren-9-one results in the disappearance of the smectic A phase and formation of the smectic C phase with the melting and clearing points significantly lower than

those of the corresponding fluorene [58,59] and dibenzopyran-6-one derivatives (compounds **4-1**, **4-2**, and **4-3**), whereas the parent biphenyl derivative **4-4** shows no mesophases. Similar trends have been reported for other cycloalkanone and cycloalkenone derivatives [63–89].

It can be proposed that the electronic and geometrical structures of cycloalkanones and cycloalkenones [10–16,40–42,44–46,49,51,56,57, 90,91] play a very important role in the intra- and intermolecular interactions [6,92–95] that affect the packing of the molecules that predominantly influences mesophase stability [92–94,96,97]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, depending on the electron density distribution in the molecular fragments under consideration, also influence the packing and hence the stability of the mesophases but play a secondary role compared to the steric factors [97]. Other molecular aspects such as the association [96] or dipole–dipole attraction in polar liquid crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [97].

STATIC DIELECTRIC PROPERTIES

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are dielectric constants that are parallel and perpendicular, respectively, to the nematic director **n**, and molecular structure of liquid crystals is described by the theory of Maier and Meier [98]:

$$\Delta\varepsilon = \mathrm{NhF}/\varepsilon_0[\Delta\alpha - \mathrm{F}\mu^2/\mathrm{kT}(1 - 3\cos^2\beta)]\mathrm{S}, \quad (1)$$

where $\mathrm{h} = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$, $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy; F is the cavity reaction field; μ is the dipole moment; β is the angle between the molecular long axis and the dipole moment; N is the number of molecules per unit volume; and S is the order parameter.

As can be seen from Table I, the positive and negative values of the dielectric anisotropy of compounds **1-1** and **1-2** are due to more pronounced contribution of the dipole moment of cyclobutanone ($\mu = 2.89$ D [16]) to the parallel and perpendicular parts of $\Delta\varepsilon$, respectively.

OPTICAL PROPERTIES

The phenomenological relation between the refractive index and the electric polarization is defined as [99,100]:

$$(\mathrm{n}^{*^2} - 1)/(\mathrm{n}^{*^2} + 2) = \mathrm{N}\alpha^*/3\varepsilon_0, \quad (2)$$

where the mean polarizability $\alpha^* = (\alpha_\parallel + 2\alpha_\perp)/3$; the mean refractive index $n^{*^2} = (n_e^2 + 2n_o^2)/3$; and n_o is the ordinary and n_e is the extraordinary refractive indices. The observed values of the optical anisotropy $\Delta n = n_e - n_o$ of compounds **1-1** and **1-2** are similar to those of other liquid crystals containing the saturated molecular fragments [101,102].

CONCLUSION

Systematic studies on the introduction of cycloalkanones and cycloalkenones into the molecular structure of liquid crystals on the creation of the mesophases and their physicochemical properties have been performed, with attempts to correlate the molecular level parameters with the observed properties. The information here presented may lead to a better understanding of the nature of liquid crystals.

REFERENCES

[1] Berthier, G. & Serre, J. (1966). In: *the Chemistry of The Carbonyl Group.*, Patai, S. (Ed.), Wiley: New York, l.
[2] Osman, M. A. & Hyunh-Ba, T. (1984). *Mol. Cryst. Liq. Cryst.*, *116*, 141.
[3] Emsley, J., Ma, L. Y. Y., Bates, P. A., & Hurthouse, M. (1988). *J. Mol. Struct.*, *178*, 297.
[4] Emsley, J., Freeman, N. J., Parker, R. J., & Overill, R. (1986). *J. Chem. Soc., Perkin Trans.*, *2*, 1479.
[5] Patai, S. (1966). *The Chemistry of the Carbonyl Group*, Wiley: New York.
[6] Zheglova, D., Denkov, N., & Kol'tsov, A. I. (1984). *J. Mol. Struct.*, *115*, 371.
[7] Riddell, F. G. (1980). *The Conformational Analysis of Heterocyclic Compounds*, Academic Press: New York.
[8] Borgers, T. R. & Strauss, H. L. (1966). *J. Chem. Phys.*, *45*, 947.
[9] Sharpen, L. H. & Laurie, V. W. (1968). *J. Chem. Phys.*, *49*, 221.
[10] Tamagawa, K. & Hilderbrandt, R. L. (1987). *J. Am. Chem. Soc.*, *109*, 1380.
[11] Smith, B. J. (1998). *J. Phys. Chem. A*, *102*, 3756.
[12] Abraham, R. J., Bovill, M. J., Chadwick, D. J., Griffiths, L., & Sancassan, F. (1980). *Tetrahedron*, *36*, 279.
[13] Bocian, D. F. & Strauss, H. L. (1977). *J. Chem. Phys.*, *67*, 1071.
[14] Dillen, J. & Geise, H. J. (1981). *J. Mol. Struct.*, *72*, 247.
[15] Cornish, T. J. & Baer, T. (1987). *J. Am. Chem. Soc.*, *109*, 6915.
[16] Berry, R. J., Waltman, R. J., Pacansky, J., & Hagler, A. T. (1995). *J. Phys. Chem.*, *99*, 10511.
[17] Poetsch, E., Binder, W., & Geelhaar, T. (1995). US Patent 5,384,072.
[18] Heckmeier, M. & Reiffenrath, V. (2000). German Pat. Appl. DE 199 55 932.
[19] Okamoto, H., Okamoto, T., Petrov, V. F., & Takenaka, S. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 719.
[20] Sucrow, W. & Radecker, G. (1988). *Chem. Ber.*, *121*, 219.
[21] Kelly, S. M., Germann, A., Buchecker, R., & Schadt, M. (1994). *Liq. Cryst.*, *16*, 67.
[22] Wilds, A. L., Shunk, C. H., & Hoffmann, C. H. (1954). *J. Am. Chem. Soc.*, *76*, 1733.
[23] Friedrich, R., Nieger, M., & Vogtle, F. (1993). *Chem. Ber.*, *126*, 1723.

[24] Sucrow, W. & Wolter, H. (1986). *Chem. Ber.*, *119*, 387.
[25] Matsunaga, Y. & Miyamoto, S. (1993). *Mol. Cryst. Liq. Cryst.*, *237*, 311.
[26] Bezborodov, V. S., Sosnovskij, G., Dabrowski, R., Dziaduszek, J., Schirmer, J., & Kohns, P. (1996). *Liq. Cryst.*, *21*, 237.
[27] Schadt, M., Buchecker, R., Leenhouts, A., Boller, A., Villiger, A., & Petrzilka, M. (1986). *Mol. Cryst. Liq. Cryst.*, *139*, 1.
[28] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., Sasnouski, G., Petrov, V. F. (1998). *Liq. Cryst.*, *24*, 647.
[29] Bezborodov, V. S., Dabrowski, R., & Dziaduszek, J. (1995). *Proc. SPIE*, *2372*, 242.
[30] Eidenschink, R. & Romer, M. (1983). *Proc 12th Freiburger Arbeitstagung Flussigkristalle*, *12*, 4.
[31] Eidenschink, R. (1983). *Mol. Cryst. Liq. Cryst.*, *94*, 119.
[32] Bezborodov, V. S., Sasnouski, G. M., Lapanik, V. I., Dabrowski, R., & Tyvorski, V. I. (2001). *Liq. Cryst.*, *28*, 1755.
[33] Saito, H., Nakagawa, E., Matsushita, T., Takeshita, F., Kubo, Y., Matsui, S., Miyazawa, K., & Goto, Y. (1996). *IEICE Trans. Electron., E79-C*, 1027.
[34] Tanaka, Y., Takatsu, H., Takeuchi, K., & Tamura, Y. (1989). Eur. Pat. Appl. EP 310 067.
[35] Bezborodov, V. S., Dabrowski, R., Sasnouski, G., & Dziaduszek, J. (1997). *Mol. Cryst. Liq. Cryst.*, *303*, 297.
[36] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., & Petrov, V. F. (1997). *Liq. Cryst.*, *23*, 69.
[37] Bezborodov, V. S. & Petrov, V. F. (1997). *Liq. Cryst.*, *23*, 771.
[38] Maier, W. & Saupe, A. (1959). *Z. Naturforsch., 14a*, 882.
[39] Gussoni, M., Rui, M., & Zerbi, G. (1998). *J. Mol. Struct.*, *447*, 163.
[40] Le Fevre, C. G. & Le Fevre, R. J. W. (1956). *J. Chem. Soc.*, 3549.
[41] Chadwick, D., Legon, A. C., & Millen, D. J. (1979). *J. Chem. Soc., Faraday Trans.*, *2*, 302.
[42] Sagear, P. & Laane, J. (1995). *J. Chem. Phys.*, *102*, 7789.
[43] Farrand, L. D., Utsumi, Y., Kagawa, H., & Kondo, K. (1996). *Liq. Cryst.*, *20*, 751.
[44] Abraham, R. J. & Lucas, M. S. (1988). *J. Chem. Soc., Perkin Trans.*, *2*, 669.
[45] Manley, S. A. & Tyler, J. K. (1970). *Chem. Commun.*, 382.
[46] Wieser, H., Smithson, T. L., & Krueger, P. J. (1982). *J. Mol. Spectr.*, *96*, 368.
[47] Laane, J. & Choo, J. (1994). *J. Am. Chem. Soc.*, *116*, 3889.
[48] Saebo, S. & Boggs, J. E. (1981). *J. Mol. Struct.*, *73*, 137.
[49] Abraham, R. J., Bergen, H. A., & Chadwick, D. J. (1982). *Tetrahedron*, *38*, 3271.
[50] Sucrow, W., Minas, H., Stegemeyer, H., Geschwinder, P., Murawski, H.-R., & Kruger, C. (1985). *Chem. Ber.*, *118*, 3332.
[51] Abraham, R. J. & Lucas, M. S. (1988). *J. Chem. Soc., Perkin Trans.*, *2*, 1269.
[52] Morin, F. G., Horton, W. J., Grant, D. M., Dalling, D. K., & Pugmire, R. J. (1983). *J. Am. Chem. Soc.*, *105*, 3992.
[53] Cereghetti, M., Marbert, R., & Scheich, K. (1982). *Helv. Chim. Acta*, *65*, 1318.
[54] Huynh-Ba, T. & Osman, M. (1989). Eur. Pat. Appl. EP 84 194.
[55] Varech, D., Lacombe, L., & Jacques, J. (1984). *Nouv. J. Chim.*, *8*, 445.
[56] Luss, H. R. & Smith, D. L. (1972). *Acta Cryst.*, *B28*, 884.
[57] Sancassan, F., Petrillo, G., & Abraham, R. J. (1995). *J. Chem. Soc., Perkin Trans.*, *2*, 1965.
[58] Witt, K. (1968). *Spectrochim. Acta, Part A, 24A*, 1115.
[59] Tanaka, M. (1976). *Bull. Chem. Soc. Jpn*, *49*, 3382.
[60] Harufuji, T., Okabe, E., Inagaki, J., Inoue, H., & Saito, H. (2000). Japan Pat. Appl. JP 2000297051.

[61] Harufuji, T., Inagaki, J., Inoue, H., Okabe, E., & Saito, H. (2001). Japan Pat. Appl. JP 2001026587.
[62] Eberson, L. & Helgee, B. (1977). *Acta Chem. Scand.*, *B31*, 813.
[63] Sasnouski, G., Bezborodov, V. S., Dabrowski, R., & Dziaduszek, J. (1999). *Mol. Cryst. Liq. Cryst.*, *332*, 227.
[64] Sasnouski, G., Bezborodov, V. S., Dabrowski, R., & Dziaduszek, J. (1998). *Proc. SPIE, 3319*, 27.
[65] Sasnouski, G., Bezborodov, V. S., Dabrowski, R., & Dziaduszek, J. (1997). *Mol. Cryst. Liq. Cryst.*, *303*, 313.
[66] Bezborodov, V. S., Dabrowski, R., Petrov, V. F., & Lapanik, V. I. (1996). *Liq. Cryst.*, *21*, 801.
[67] Bezborodov, V. & Lapanik, V. (1997). *Mol. Cryst. Liq. Cryst.*, *302*, 315.
[68] Tykarski, W., Dziaduszek, J., Dabrowski, R., & Bezborodov, V. (1998). *Proc. SPIE, 3319*, 31.
[69] Wang, Q., Fan, S. Y., Wong, H. N. C., Li, Z., Fung, B. M., & Nguyen, H. T. (1993). *Tetrahedron*, *49*, 619.
[70] Stegemeyer, H., Meister, R., Ellermann, K. H., Altenbach, H. J., & Sucrow, W. (1992). *Liq. Cryst.*, *11*, 667.
[71] Bezborodov, V. S., Lapanik, V. I., & Sasnouski, G. M. (2002). *Liq. Cryst.*, *29*, 521.
[72] Bezborodov, V. S., Sasnouski, G., & Lapanik, V. I. (2000). *Liq. Cryst.*, *27*, 935.
[73] Bezborodov, V. S., Sasnouski, G. M., & Lapanik, V. I. (2001). *Liq. Cryst.*, *28*, 897.
[74] Bezborodov, V. S., Dabrowski, R., Dziaduszek, J., Czuprynski, K., & Raszewski, Z. (1996). *Liq. Cryst.*, *20*, 1.
[75] Sasnouski, G., Bezborodov, V., Dabrowski, R., & Dziaduszek, J. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 63.
[76] Bezborodov, V, Lapanik, V., & Sasnouski, G. (2000). *Ferroelectrics*, *243*, 49.
[77] Lauk, U. H., Skrabal, P., & Zollinger, H. (1985). *Helv. Chim. Acta*, *68*, 1406.
[78] Brettle, R., Dunmur, D. A., Farrand, L. D., & Marson, C. M. (1996). *J. Mater. Chem.*, *6*, 747.
[79] Hird, M., Toyne, K. J., Slaney, A. J., Goodby, J. W., & Gray, G. W. (1993). *J. Chem. Soc., Perkin Trans.*, *2*, 2337.
[80] Bullock, P. J., Byron, D. J., Harwood, D. J., Wilson, R. C., & Woodward, A. M. (1984). *J. Chem. Soc., Perkin Trans.*, *2*, 2121.
[81] Takatoh, K., Sunohara, K., & Sakamoto, M. (1988). *Mol. Cryst. Liq. Cryst.*, *164*, 167.
[82] Takatoh, K. & Sakamoto, M. (1990). *Mol Cryst., Liq. Crys.*, *182*, 339.
[83] Petrov, V. F. & Pavluchenko, A. I. (2003). *Mol. Cryst. Liq. Cryst.*, *393*, 1.
[84] Geschwinder, P., Minas, H., & Sucrow, W. (1985). *Chimia*, *39*, 186.
[85] Clarke, M. F. & Owen, L. N. (1949). *J. Chem. Soc.*, 320.
[86] Buchecker, R., Lukac, T., & Reichnard, J. (1999). PCT WO 99/12920.
[87] Kinsho, T., Shimizu, T., Ogihara, T., & Nakashima, M. (1995). Eur. Pat. Appl. EP 687 678.
[88] Kinsho, T., Shimizu, T., Ogihara, T., & Nakashima, M. (1996). Eur. Pat. Appl. EP 711 777.
[89] Tamura, Y., Takatsu, H., Sasaki, M., & Takeuchi, K. (1998). Japan Pat. Appl. JP 10147549.
[90] Svendsen, E. N. & Vala, M. T. (1972). *Acta Chem. Scand.*, *26*, 3475.
[91] Bouchoux, G., Leblanc, D., Mo, O., & Yanez, M. (1997). *J. Org. Chem.*, *62*, 8439.
[92] Osman, M. A. (1983). *Z. Naturforsch.*, *38a*, 693.
[93] de Jeu, W. H. (1983). *Phil. Trans. R. Soc. A*, *309*, 217.
[94] Ostrovskii, B. I. (1999). In: *Structure and Bonding, Mingos*, D. M. P. (Ed.), Springer Verlag: New York, Vol. 94, 200.

[95] Wiberg, K. B. & Martin, E. (1985). *J. Am. Chem. Soc.*, *107*, 5035.
[96] Schand, Hp. & Osman, M. A. (1981). *J. Chem. Phys.*, *75*, 880.
[97] Osman, M. A. & Revesz, L. (1982). *Mol. Cryst. Liq. Cryst., Lett.*, *82*, 41.
[98] Maier, W. & Meier, G. (1961). *Z. Naturforsch., 16a*, 262.
[99] de Jeu, W. H. (1980). *Physical Properties of Liquid Crystalline Materials*, Gordon & Breach: New York.
[100] de Jeu, W. H., Gerristma, C. J., van Zanten, P., & Goosens, W. A. (1972). *Phys. Lett., 39A*, 355.
[101] Petrov, V. F., Torgova, S. I., Karamysheva, L. A., & Takenaka, S. (1999). *Liq. Cryst.*, *26*, 1141.
[102] Petrov, V. F., Duan, M., Okamoto H., Mu, J., Shimizu, Y., & Takenaka, S. (2001). *Liq. Cryst.*, *28*, 387.