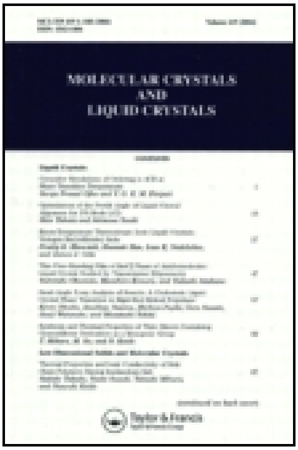

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Low Melting Nematics 2-Chloro-4-Alkylphenyl 4-Alkylbicyclo-[2,2,2]Octane-1-Carboxylates with Negative Dielectric Anisotropy

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To cite this article: Roman Dabrowski, Jan Jadżyn, Sławomir Czerkas, Jerzy Dziaduszek & Andrzej Walczak (1999): New Low Melting Nematics 2-Chloro-4-Alkylphenyl 4-Alkylbicyclo-[2,2,2]Octane-1-Carboxylates with Negative Dielectric Anisotropy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 61-68

To link to this article: http://dx.doi.org/10.1080/10587259908023744

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 61-68
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New Low Melting Nematics 2-Chloro-4-Alkylphenyl 4-Alkylbicyclo-[2,2,2]Octane-1-Carboxylates with Negative Dielectric Anisotropy

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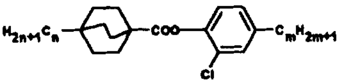
Synthesis of a new class of stable, low melting nematics with a negative dielectric anisotropy is described. The basic physical properties of 2-chloro-4-heptylphenyl 4-pentylbicyclo-[2,2,2]octane-1-carboxylate (7CP5BOC) are presented.

Keywords: low melting nematics; viscosity; dielectric constants; refractive indices; synthesis of esters

INTRODUCTION

Many stable nematic liquid crystals with a positive dielectric anisotropy and the mesophase at the room temperature are known and used. The most popular are the pentylcyanobiphenyl (5CB)[1] and 4-trans-4-hexylcyclohexylisothiocyanatobenzene (6CHBT)[2]. Nematics with a negative dielectric anisotropy are much less numerous. The best known compound of this type is MBBA[3], which is, however, not thermally stable and somewhat chemically active. Here, we present a new class of nematics, 2-chloro-4-alkylphenyl esters of 4-alkylbicyclo[2,2,2]octane-1-carboxylic acids, with a negative dielectric anisotropy:



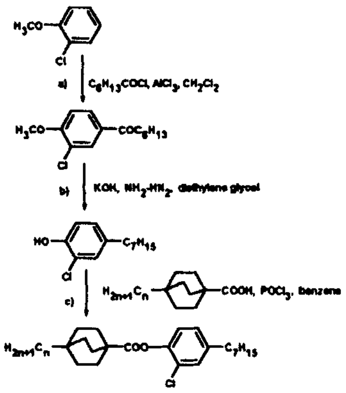
(1)

Some of the derivatives (1) are nematics at room temperature with the clearing point about 40°C. The high thermal stability of the nematic phase in (1) is due to the bicyclo[2,2,2]octane ring which balances the depression of the clearing temperature caused by the lateral substitution of the chlorine atom in benzene ring of (1).

EXPERIMENTAL

Synthesis

The esters (1) were produced by the following route showed in the scheme.



It is the worth to note, that in the Huang-Milong reaction condition (stage b) not only the carbonyl group was reduced, but simultaneously the substitution of CH_3O group by OH one took place, and not the expected 2-chloro-4-heptylanisole but the desired 2-chloro-4-heptylphenol was formed in the same stage. The preparation procedure is given for 2-chloro-4-heptylphenyl ester of

4-pentylbicyclo[2,2,2]octane-1-carboxylic acid (7CP5BOC), which has a general character.

Stage a - 2-chloro-4-heptanoylanisole

Anhydrous $AlCl_3$ (160.2 g, 1.2 mol) and methylene chloride (1 dm^3) was cooled to 0°C and heptanoyl chloride (163.4 g, 0.1 mol) was dropped and then 2-chloroanisole (142.5 g, 1 mol) was added; the temperature was kept between 0-5°C. The mixture was stirred for further three hours and then it was poured into iced water (5 dm^3). The CH_2Cl_2 layer was separated, washed with water (three times), dried over anhydrous sodium sulfate and filtrated. The solvent was distilled off, and the residual oil was crystallized from methanol (500 cm^3) cooling the solution to -20°C. 193 g (75 %) of the end product was obtained, m.p. 30.5-31°C; purity 99.3% (G.C); IR: (CCl_4) 1687 cm^{-1} (C=O); NMR: (200 MHz) $^1H_1$ δ 2.90 (t 2H, J=7.5 Hz $COCH_2$), 3.97 (s 3H, CH_3O), in the benzene ring: 6.97 (d, J=8.5 Hz 1H), 7.872 and 7.884 (two doublet, J=8.6 Hz 1H): 7.992 and 8.003 (two singlet, 1H) MS:m/e 226 (m) with 228 (w) (M^+), 141 with 143 (3:1 ratio of intensity, CH_2-Ph-Cl(OH)$^+$).

Stage b - 2-chloro-4-heptylphenol

The mixture of 2-chloroheptanoylanisole (165 g, 0.65 mol), 80 % hydrazine hydrate (121.5 g, 1.95 mol), diethylene glycol (800 cm^3) and KOH (145 g, 2.6 mol) was refluxed for 3 hours with stirring and then volatile components were distilled off until 200°C was reached and heating was continued for further 5 hours. The mixture was cooled to the room temperature, then diluted with water to the total volume of 2 dm^3 and concentrated hydrochloric acid (500 cm^3) was added. The product was extracted with toluene (3x200 cm^3). The combined extracts were washed with water (3 times) and dried over anhydrous $MgSO_4$. Toluene was distilled off, and the residual oil was distilled under the reduced pressure (0.02 kPa). The fraction boiling at 114°C was collected in the amount of 110 g (75 %); purity 98% (G.C); IR: (CCl_4) dimeric form (3552 cm^{-1}) and monomeric form (3608 cm^{-1}) of OH group; MS:m/e 226 (m) with 228 [M^+]; 141 (s) with 143.

Stage c - 2-chloro-4-heptylphenyl 4-pentylbicyclo[2,2,2]octane-1-carboxylate

The mixture of 4-pentylbicyclo[2,2,2]octane-1-carboxylic acid (11.2 g, 0.05 mol) prepared according to Ref.[4], 2-chloro-4-heptylphenol (11.3 g, 0.05 mol), benzene (10 cm^3) and $POCl_3$ (3.06 g, 0.06 mol) was refluxed for 5 hours. Then the mixture was cooled to the room temperature, diluted with benzene and poured into water. The benzene layer was separated, washed with water (3 times) and dried over anhydrous $MgSO_4$. The solvent was distilled off and the crude product was crystallized from the mixture: methanol (350 cm^3) and THF (30 cm^3) and then was purified by silica gel column chromatography using hexane as an eluent. The separated product was recrystallized from methanol: THF mixture (170 cm^3:40 cm^3), 12 g of the final product was obtained, 56 % yield, purity 99.5 % (G.C.), phase transition: Cr 18.2 N 43.5 I; IR:(CCl_4 and film) 1758 cm^{-1} (-COO-); 1214 and 1195 cm^{-1} (-COO-); NMR: $^1H_1$ δ 2.50 (t 2H, CH_2-Ph); 6.9-7.2 (m, 3H); MS:m/e 226 (w); 207 (m) $(C_5H_{11}C_8H_{10})^+$, 179 (s) $(C_5H_{11}C_8H_{10}CO)^+$, 141 (m).

Apparatus

Static dielectric permittivities $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ were measured at 1kHz using a Wayne-Kerr 6425 bridge. The liquid crystal sample (0.6 mm thickness) was placed within a plane copper capacitor with gold covered electrodes. A magnetic field B=0.6T was used to orient the sample in the nematic phase. The permittivity components $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ of the ordered nematic were measured with the electric field **E** parallel and perpendicular to **B**, respectively. The obtained accuracy of permittivity measurements was about 0.1% and the temperature was stabilized within ±0.01°C. The refractive indices were measured by means of an appropriately prepared Abbe refractometer for λ=589 nm. The accuracy of Δn_o=0.0002 and Δn_e=0.0005. The elastic constants have been determined in a new method using a tunable waveguide with the alignment nematic[5]. Density measurements were carried out with an A. Paar DMA 60/602 vibration tube densitometer with an accuracy of $5 \cdot 10^{-5}$g/cm^3. Viscosity was determined with a Haake viscometer Rotovisco RV20 with measuring system CV100, the share rate being 275s^{-1}. The sensor system was of Mooney-Ewart type (ME15). The measuring system was thermostated to ±0.05°C using a Haake F3 ultrathermostat. The viscosity data were reproducible to ±0.5%. Viscosity was also measured with a capillary viscometer. The accuracy was about ±1%.

RESULTS AND DISCUSSION

The phase transition temperatures (upper line) and enthalpies (kJ/mol bottom line) are as follow:

n=3	7CP3BOC	Cr$_1$ 6.4 Cr 37.2 (N 31.1) I
		2.4 19.7 0.5
n=5	7CP5BOC	Cr$_1$ 7.9 Cr 18.2 N 43.5 I
		0.8 21.7 0.8
n=7	7CP7BOC	Cr 14.1 N 47.8 I
		18.5 1.0

7CP5BOC and 7CP7BOC can be cooled to -30°C without crystallization.

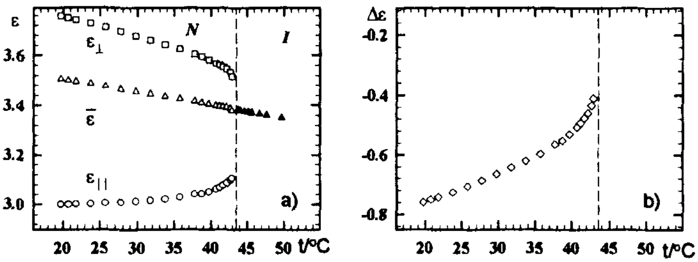


FIGURE 1 Permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ and $\bar{\varepsilon}$ (a), and dielectric anisotropy $\Delta\varepsilon$ (b) *vs.* temperature for 7CP5BOC.

Fig. 1 presents the temperature dependencies of the principal permittivities $\varepsilon_\|$ and $\varepsilon_\perp$, mean permittivity $\bar{\varepsilon} = \frac{1}{3}(\varepsilon_\| + 2\varepsilon_\perp)$ and dielectric anisotropy $\Delta\varepsilon = \varepsilon_\| - \varepsilon_\perp$ for 7CP5BOC. The compound shows a negative dielectric anisotropy; at 22°C, $\Delta\varepsilon = -0.7$. The change of the mean value of permittivity $\bar{\varepsilon}$ at the isotropic-nematic phase transition temperature can be neglected, only small change in the slope of the temperature dependence of $\bar{\varepsilon}$ and ε_{iso} is observed ($\partial\varepsilon_{iso}/\partial t = -5.042\cdot10^{-3}$, $\partial\bar{\varepsilon}/\partial t = -5.059\cdot10^{-3}$).

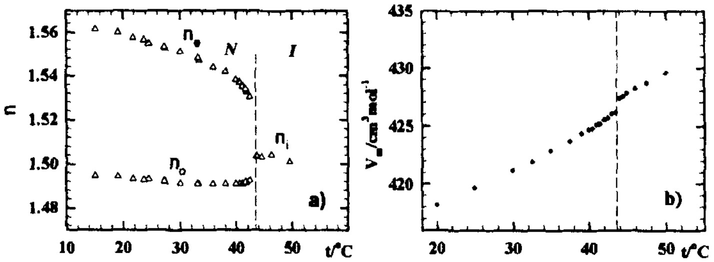


FIGURE 2 Temperature dependence of the refractive indices (a) and the molar volume (b) of 7CP5BOC.

Fig. 2a. presents the temperature dependence of the ordinary n_o and extraordinary n_e indices of 7CP5BOC; $\Delta n = 0.0642$ at 22°. Fig. 2b presents its temperature dependence of the molar volume. At the isotropic-nematic phase transition temperature a V_m increase of about 1.2 cm^3/mol is observed. The density for different temperatures may be calculated from: $d(t) = d_o + \alpha \cdot t$, where d_o and α are respectively 1.0504 and -7.4586 in the nematic phase or 1.0545 and -9.2673 in the isotropic phase.

Fig. 3 shows the temperature dependence of the viscosity of 7CP5BOC. The results obtained by two different methods: *i*) with the rotational viscometer (dynamic viscosity) and *ii*) with the capillary viscometer (kinematic viscosity) agree well with each other. The kinematic viscosity ν and dynamic viscosity η are linked through the density ρ:

$$\nu = \eta/\rho$$

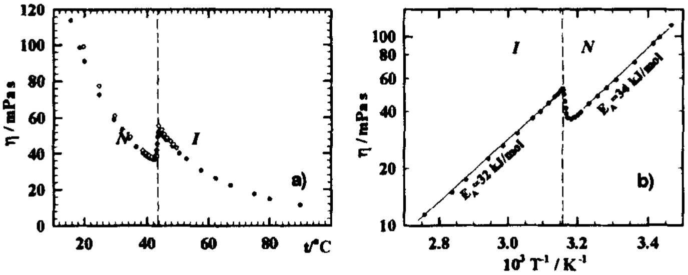


FIGURE 3 Temperature dependence of the dynamic viscosity of 7CP5BOC. Full points refer to the rotational viscometer, open points - to the capillary viscometer.

The physical properties of 7CP5BOC and MBBA are compared in Table I

TABLE I The comparison of physical properties of 7CP5BOC and MBBA

	7HCP5BOC	MBBA
1. Melting point, [°C]	18.2	22,0[6]
2. Clearing point, [°C]	43.5	48,0[6]
3. Dipole moment [D]	1.92 (50°C)	0.78[7]
4. Density $[g{\cdot}cm^{-3}]$	1.0340	1.041[8]
5. Dielectric permittivity:		
$\varepsilon_{\parallel}$	3.00	4.42[8]
$\varepsilon_{\perp}$	3.74	4.98[8]
$\Delta\varepsilon$	-0.71	-0.56[8]
6. Refractive indices [λ_o=589 nm]:		
n_e	1.5574	1.791
n_o	1.4932	1.548[9]
Δn	0.0064	0.244[9]
7. Elastic constants:		
k_{11} $[10^{-12}N]$	7.2±3	6.95[10]
k_{22} $[10^{-12}N]$	-	4.4[10]
k_{33} $[10^{-12}N]$	5.6±2.4	8.99[10]
8. Dynamic viscosity [mPa·s]:	83	31[11]
9. Activation energy of dynamic viscosity [kJ/mol]:		
nematic phase	32	27.6[11]
isotropic phase	34	32.5[11]
10. Order parameter S	0.63	0.580[8]

Samples with $T_{N\text{-}I}$=45°C and 47°C, 46°C and 40°C were tested in Ref.[8,9,10,11] respectively.

Compound 7CP5BOC has similar dielectric properties to MBBA but its viscosity is higher and its birefringence is lower. These new compounds owing to their high chemical stability and the convenient range of the nematic phase may be used as a single compound for a demonstration of different liquid crystal properties in which a negative anisotropy is significant. The presence of a chlorine atom in the lateral position provides a good solubility for polar as well as unpolar compounds. For this reason we propose to use these new compounds as anisotropic solvents for spectroscopic and kinetic studies.

Acknowledgments

This work was supported by the Polish Committee for Scientific Research under ZNS 168.

References

[1] G.W. Gray, K.J. Harrison, J.A. Nash, J. Constant, D.S. Hulmes, J. Kitton and E.R. Raynes, *Liquid Crystals and Ordered Fluides*, ed. J.W. Johnson, R. S. Porter, (Plenum Press New York, 1974).

[2] R. Dąbrowski, J. Dziaduszek and T. Szczuciński, *Mol.Cryst.Liq.Cryst.*, **124**, 241 (1985).

[3] H. Kelker and B. Scheurle, *Angew.Chem.*, **8**, 903 (1969).

[4] P. Adomenas, G.V. Mazhunajtis and D.K. Girjunaite, Zh.Org.Khim, **19**, 2366 (1983).

[5] A. Walczak, E. Nowinowski-Kruszelnicki and A. Kieżun, *SPIE*, **3318**, 344 (1997).

[6] M. Sorai, T. Nakamura and S. Seki, *Pranama Suppl.*, **1**, 503 (1975).

[7] J.W. Baran, J. Kędzierski, Z. Raszewski and J. Żmija, *Electron Technol.*, **12**, 107 (1979).

[8] Z. Raszewski, Ph.D. Thesis, Military University of Technology (1978).

[9] I. Haller, H.A. Huggins and M.J. Freiser, *Mol.Cryst.Liq.Cryst.*, **16**, 53 (1972).

[10] W.H. de Jeu, W.A.P. Claassen and M.J. Spruijit, *Mol.Cryst.Liq.Cryst.*, **37**, 107 (1979).

[11] A.E. White, P.E. Cladis and S. Torza, *Mol.Cryst.Liq.Cryst.*, **43**, 13 (1979).