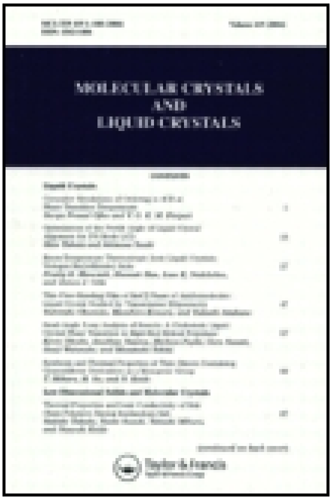


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

New Liquid Crystalline Tetrahydropyran Derivatives

Atsuko Fujita [a], Tokifumi Masukawa [a], Subaru Kawasaki [a] & Dietrich Demus [b]

[a] Chisso Petrochemical Corporation, Research Center, Ichihara, Chiba, Japan

[b] International Scientific Consulting Office, Halle, Germany

To cite this article: Atsuko Fujita, Tokifumi Masukawa, Subaru Kawasaki & Dietrich Demus (2009) New Liquid Crystalline Tetrahydropyran Derivatives, Molecular Crystals and Liquid Crystals, 509:1, 245/[987]-262/[1004], DOI: 10.1080/15421400903065705

To link to this article: http://dx.doi.org/10.1080/15421400903065705

Mol. Cryst. Liq. Cryst., Vol. 509, pp. 245/[987]–262/[1004], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903065705

New Liquid Crystalline Tetrahydropyran Derivatives

Atsuko Fujita[1], Tokifumi Masukawa[1], Subaru Kawasaki[1], and Dietrich Demus[2]
[1]Chisso Petrochemical Corporation, Research Center, Ichihara, Chiba, Japan
[2]International Scientific Consulting Office, Halle, Germany

We synthesized new low polar derivatives of tetrahydropyran with nematic and smectic behaviour. Quantum chemical calculations show, that the most elongated conformers of the cyclohexane and tetrahydropyran derivatives have nearly identical molecular shape. The different liquid crystalline behaviour can be explained by different amounts of conformers deviating from the most elongated shape. The $\Delta\varepsilon$ *and* Δn *have been calculated and compared with the experimental data obtained by extrapolation from basic mixtures. The two-ring compounds dissolved in the basic mixture have low order parameters and excellent solubility. By linear extrapolation, the two-ring compounds possess negative viscosities, but positive by logarithmic extrapolation.*

Keywords: nematics; quantum chemical calculations; synthesis; tetrahydropyrans; viscosity; $\Delta\varepsilon$ and Δn

1. INTRODUCTION

In order to meet the requirements of the recent powerful development of Liquid Crystal Display (LCD) devices, liquid crystal materials for the LCD application are needed which have improved properties [1]. To satisfy these requirements, enormous numbers of liquid crystal materials are investigated, especially with respect to better properties of the quality of liquid crystal mixtures, dielectric anisotropy ($\Delta\varepsilon$), optical birefringence (Δn), nematic temperature range and viscosity.

Basically, $\Delta\varepsilon$ and Δn of the liquid crystal mixture can be roughly estimated from the additivity rule of the single compounds, and for the latter they are predictable from the molecular structure with quantum chemical calculation methods [2]. On the contrary, it is

Address correspondence to Atsuko Fujita, Chisso Petrochemical Corporation, Goi Research Centre, Research Center 1, 5-1 Goikaigan, Ichihara, Chiba 290-8551, Japan. E-mail: afujita@chisso.co.jp

difficult to predict nematic temperature range, viscosity and solubility properties at lower temperature and these factors are sometimes deciding the LCD display quality.

Liquid crystalline compounds having a tetrahydropyran structure are already known [3]. In most cases the tetrahydropyran ring is directly connected with a benzene ring.

We synthesized new tetrahydropyran derivatives without direct connection to aromatic rings and found that they have better solubility and lower melting temperatures in comparison to their carbon analogues, the cyclohexane derivatives.

In this paper, we discuss the differences of the thermal behaviour of the tetrahydropyran and cyclohexane derivatives from the viewpoint of conformational differences. Furthermore, the $\Delta\varepsilon$ and Δn have been calculated and compared with the experimental data obtained from different basic mixtures. By linear extrapolation from the mixtures the two-ring compounds show negative viscosities, which are positive, however, by logarithmic extrapolation. The compounds are valuable components for mixtures to be used in LCDs.

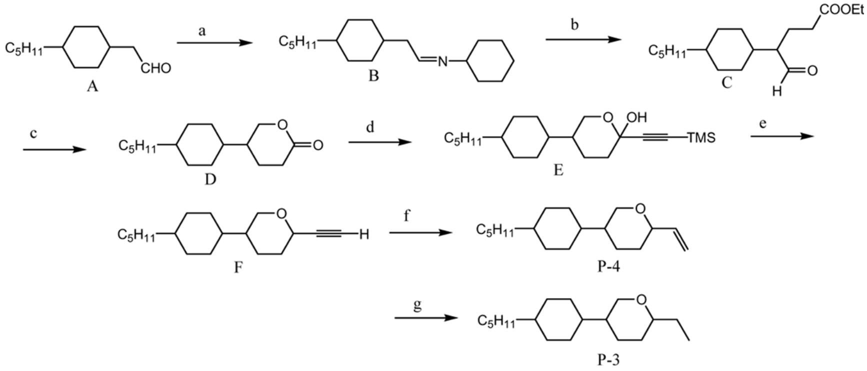
2. SYNTHESIS AND TRANSITION TEMPERATURES OF TETRAHYDROPYRAN DERIVATIVES

2.1. Synthesis of 2-Substituted Tetrahydropyran Derivatives

The typical procedure for synthesis of straight carbon chain group substituted at the 2- position of tetrahydropyran derivatives is shown in Scheme 1. The desired cyclohexyl tetrahydropyran derivative, P-3, was synthesized from the cyclohexyl acetaldehyde derivative (A). Condensation of Compound **A** with cyclohexyl amine gave the imine derivative (B). It was reacted with ethyl acrylate under Michael addition condition to give the formyl ester derivative (C), and the following selective reduction of the formyl group with $NaCNBH_3$ gave cyclohexyl lactone (D) which was converted into a hemiacetal through the reaction with trimethyl silyl lithium acetylide. After removal of the trimethyl silyl group by the usual method, hydrosilylation reaction of a hemiacetal and the following selective hydrogenation reaction using Lindlar catalyst gave vinyl tetrahydropyran derivative (P-4) and palladium carbon catalyst yielded the saturated compound (P-3).

2.2. Synthesis of 2,5-dicyclohexyl Tetrahydropyran Derivatives

The typical procedure of synthesis of 2,5-dicyclohexyl tetrahydropyran derivatives is shown in Scheme 2. A hydroxy ester (I) was obtained

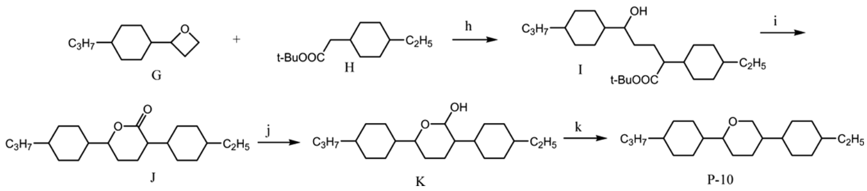


SCHEME 1 Synthesis of 2-alkyl or alkenyl tetrahydropyran a; Cyclohexylamine, Et_2O, r.t., b; Ethyl acrylate, reflux, 10 hrs, c; $NaCNBH_3$, pH 3, d; Trimethylsilylacetylene, n-BuLi, e; Et_3SiH, $Et_2O\text{-}BF_3$, CH_2Cl_2, f; H_2, Lindlar cat., g; H_2, Pd-C/cat.

from the reaction between the oxetane derivative (G) and the lithiated intermediate of t-butyl cyclohexyl acetate (H) in the presence of the boron trifluoride etherate complex. Intramolecular esterification of **I** under acidic condition gave 2,5-disubstituted lactone (J) in good yield. Diisobuthylaluminium hydride reduction of lactone (J), and following hydrosilylation of the hemiacetal finally yielded the desired tetrahydropyran compound (P-10).

2.3. Measurement Conditions and Instruments

^{1}H-NMR: Bruker DRX 500 (500 MHz); δ (ppm) = 7.26 for chloroform. Transition temperature: Perkin Elmer Diamond DSC differential scanning calorimetry and Nikon Optiphot polarizing microscopy with a Mettler Toledo FP82HT hot stage. $\Delta\varepsilon$ and elastic constants at 25°C: Hewlett Packard 4284A LCR meter. Δn at 25°C: Atago 4 T and 2 T Abbe refractometer. Rotational viscosity ($\gamma 1$) at 25°C: TOYO Corporation TCM-1.



SCHEME 2 Synthesis of 2,5-dicyclohexyltetrahydropyran h; LDA, $Et_2O\text{-}BF_3$, CH_2Cl_2, i; TFA, CH_2Cl_2 j;DIBAL, −60°C, k; Et_3SiH, $Et_2O\text{-}BF_3$.

2.4. Phase Transitions of the New Compounds

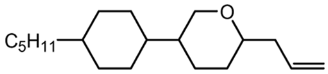
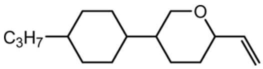
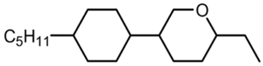
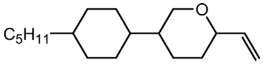
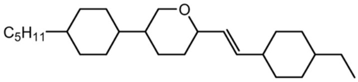
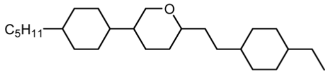
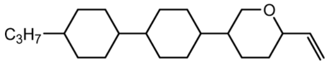
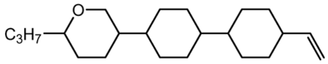
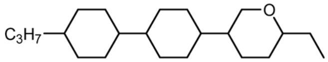
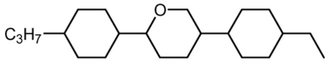
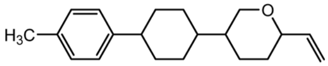
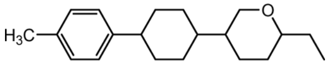
The phase transition temperatures and transition enthalpies are listed in Table 1. The two-ring tetrahydropyran derivatives, P-1 to P-4, have mesomorphic temperature ranges at around room temperature. In particular, compounds having a vinyl side chain, P-2 and P-4, show wider nematic temperature ranges and lower melting temperatures. From the comparison of compounds P-3 and P-4, P-7 and P-9, and P-11 and P12, it is obvious that the vinyl substituent in terminal position of the compounds induces stabilized nematic phases. In order to compare the properties of the non-polar tetrahydropyran derivatives in Table 1, the phase transitions of analogous cyclohexane derivatives are collected and listed in Table 2. In general, the analogous cyclohexane derivatives possess higher clearing temperatures and the substitution of the vinyl group instead of the ethyl group causes the appearance of the nematic phases. However, in the most cases of cyclohexane derivatives, the smectic B phase is retained. Compound R-7 and R-8 having the methoxy group are well known as compounds which can preserve the nematic phase when they are used in nematic mixtures [10(b)]. From the above comparison, it is confirmed that the combination of the tetrahydropyran ring and vinyl groups results in a strong tendency to exhibit the nematic phase.

The compounds having the tetrahydropyran ring and a linkage group in the central position of the molecule possess higher melting temperatures and hardly exhibit mesomorphic properties.

3. MOLECULAR SHAPE AND CONFORMERS OF TETRAHYDROPYRAN DERIVATIVES

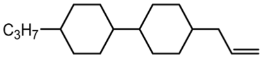
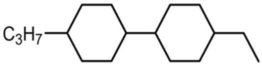
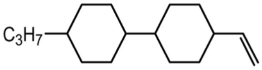
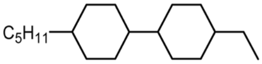
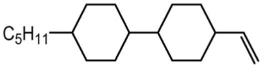
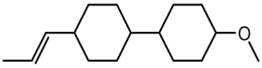
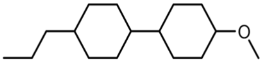
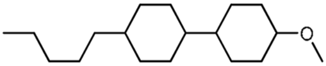
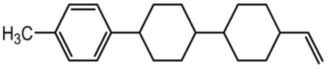
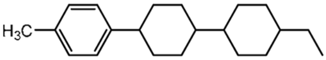
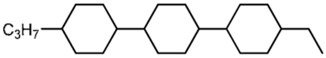
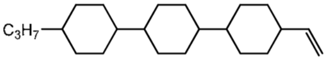
The tetrahydropyran derivatives possess an elongated molecular shape, suited for formation of liquid crystalline phase. Comparing them with cyclohexane derivatives, in all cases analogous tetrahydropyran derivatives show lower clearing temperatures. In order to find out the reason for this behaviour, we calculated the molecular structures optimised by quantum chemical methods (semi-empirical method, CAChe/PM5 [14]). Figure 1 shows the optimised molecular shapes of compounds P-3 and R-4. The molecular length and molecular breadth, which in non-polar compounds substantially control the clearing temperature, are nearly identical. The existence of enantiomers arising from the chirality of the tetrahydropyran ring could be considered as substantial difference. Generally, optically active substances can have quite different phase transition temperatures compared with racemates. However, we have not been able to separate optically pure compounds.

TABLE 1 Phase Transitions of the Tetrahydropyran Derivatives

		Phase transition	
Structures		Temperature (°C)	Enthalpy (kJ/mol)
P-1		C -1.9 SmB 56.5 I	C 12.6 SmB 5.4 I
P-2		C 8.2 N 24.6 I	C 15.3 N 0.41 I
P-3		C -14.1 SmB 45.7 I	C 6.1 SmB 4.3 I
P-4		C 1.5 N 46.0 I	C 15.8 N 0.45 I
P-5		C 197.8 I	C 13.4 I
P-6		C 174.6 I	C 15.4 I
P-7		C 206.8 N 221.2 I	C 9.3 N 0.82 I
P-8		C 202.7 N 204.8 I	C 10.2 N 0.53 I
P-9		C 223.2 I	C 12.9 I
P-10		C 6.8 SmB 199.3 I	C 10.8 SmB 11.3 I
P-11		C 68.9 N 142.7 I	C 18.5 N 0.53 I
P-12		C 77.4 N 115.3 I	C 20.1 N 0.4 I

Another difference of the compounds is the right ring, which may influence the conformation of the right substituent. In order to check this hypothesis we calculated the relaxed energy map of the rotations

TABLE 2 Phase Transitions of the Cyclohexane Derivatives

			Phase transition	
Structures		Ref.	Temperature (°C)	Enthalpy (kJ/mol)
R-1		[4]	C 6.4 N 70.1 I	C 18.0 N 6.2 I
R-2		[5]	C −6.3 SmB 66.8 I	C 13.8 SmB 6.41I
R-3		[6]	C −23.9 SmB 33.9 N 48.6 I	C 6.48 SmB 3.29 N 0.46 I
R-4		[7]	C -6.28 SmB 77.7 I	C 17.7 SmB 6.86 I
R-5		[8]	C -7.5 SmB 52.6 N 64.0 I	C 18.3 SmB 3.95 N 0.52 I
R-6		[9]	C 6.1 N 21.1 I	C 18.3 N 0.52 I
R-7		[10]	C 13.8 (SmB 11.2) N 20.8 I	C 17.1 (SmB 2.82) N 0.45 I
R-8		[10]	C 12.1 SmB 28.4 N 37.6 I	C 19.8 SmB 3.15 N 0.52 I
R-9		[11]	C 63.8 N 159.9 I	C 24.0 N 0.67 I
R-10		[12]	C 64.6 SmB 105.5 N 145.3 I	C 17.35 SmB 4.29 N 0.58 I
R-11		[13]	C 70.2 SmB 220.1 I	–
R-12		[13]	C 227.4 SmB 233.4 I	C 10.0 SmB 0.6 I

around the single bond of the right substituent (bond a in Fig. 1). The result is displayed in Figure 2. We see that the energy maxima and minima are practically in the same positions. The major differences are the heights of the maxima at 0 and the minima at −172° and −65°.

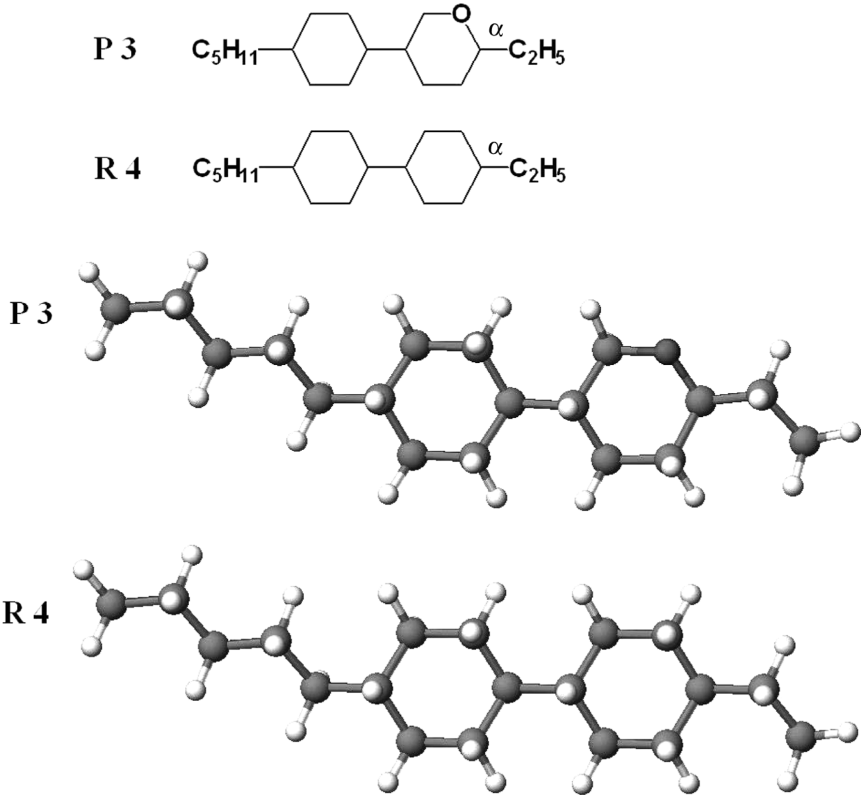


FIGURE 1 Comparison of the molecular structure of a tetrahydropyran and a cyclohexane derivative.

In the Boltzmann distribution the different conformers exist in amounts depending on their relative energies.

The Boltzmann distribution has been calculated [15] using the formula

$$x_i = \frac{\exp\left(\frac{-HOF_i}{k_B T}\right)}{\sum_i \exp\left(\frac{-HOF_i}{k_B T}\right)} \tag{1}$$

x_i = molar fraction of the conformer i; in the following the existence probability

EP = 100 x_i has been used.

HOF_i = Heat of Formation of a conformation

k_B = Boltzmann constant

T = temperature, here we used room temperature 298.2 K.

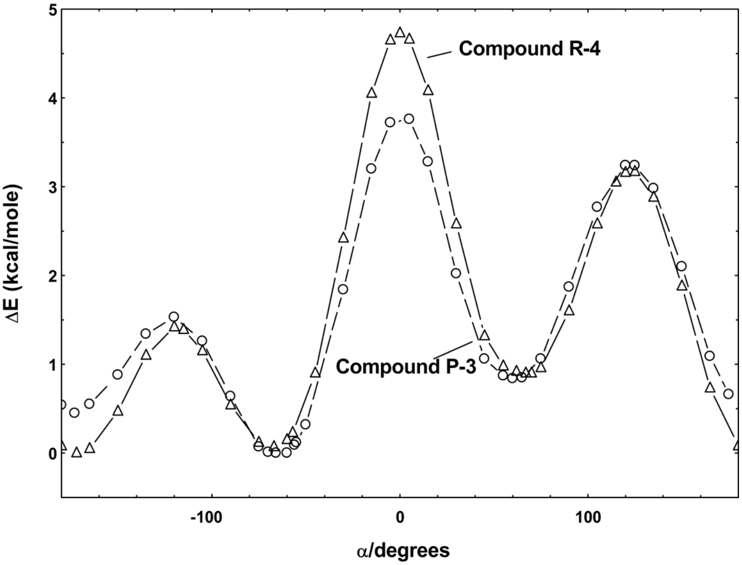


FIGURE 2 Energy maps of the rotation of the right substituent of compounds P-3 and R-4 around the single bond. Relaxed energies calculated with PM5.

The molecular breadth in all cases is the breadth of the cyclohexane ring B = 6.73 Å.

Table 3 shows that the most elongated conformer of compound P-3 is not the most stable one. The most stable conformer P-3c is less elongated, but has the highest existence probability. Contrary to that, in compound R-4 the most stable conformer R-4 at the same time is the most elongated and has the highest L/B. Because the clearing temperatures sensitively depend on L/B, the data of Table 3

TABLE 3 Properties of the Different Conformers of Compounds P3 and R4

Compound/ conformer	α (°)	HOF (kcal/mole)	L (Å)	L/B	EP (%)
P-3	−172.94	−127.7065	20.06	2.98	25.07
P-3b	60.04	−127.4823	19.17	2.84	17.17
P-3c	−65.84	−128.2011	19.56	2.91	57.56
P-4	−171.95	−100.7215	20.20	3.00	58.33
P-4b	−61.75	−100.1116	19.55	2.90	20.84
P-4d	62.04	−100.1116	19.55	2.90	20.84

L = molecular length.
B = molecular breadth.

elucidate why the tetrahydropyran derivatives possess lower clearing temperatures than analogous cyclohexane derivatives.

4. PHYSICAL PROPERTIES OF THE NEW COMPOUNDS

4.1. Solubility of the Tetrahydropyran Derivatives

Compared with other low polar compounds, the tetrahydropyran derivatives exhibit relatively large solubility in mixtures. As a first approximation, the solubility can be calculated by the Schroeder-van Laar equation

$$\ln x_i = -\frac{\Delta H_{0i}}{R}\left(\frac{1}{T} - \frac{1}{T_{0i}}\right) \tag{2}$$

T = actual temperature
ΔH_{0i} = melting enthalpy of the pure compound i
T_{0i} = melting temperature of the pure compound i
x_i = molar fraction of the compound i
R = universal gas constant

This equation teaches that the solubility of a compound is the higher, the lower are ΔH_{0i} and T_{0i}. Comparing the tetrahydropyran derivatives of Table 1 with the cyclohexane derivatives of Table 2 we see that the melting temperatures in general are not very different, but the melting enthalpies of the former are smaller. Melting enthalpies of not more than about 15 kJ/mole for three-ring compounds (Table 1 P-5 to P-10) are unusually small.

4.2. Order Parameters, Dielectric and Optical Data

In order to explain physical data like $\Delta\varepsilon$ and Δn of mixtures, we need the knowledge of the order parameter of mixtures. Compounds dissolved in a basic mixture may have the same order parameter as the basic mixture, when the molecules are very similar. However, when the dissolved molecules are different concerning geometry or chemical nature, their order parameter can be smaller or larger [16]. Because optical data can be measured and calculated with higher accuracy than dielectric data, we use the comparison of measured and calculated optical data for the determination of the order parameters of selected compounds.

The equation for the dielectric constant ε of isotropic media has been derived by Onsager [17].

$$\varepsilon = 1 + (\mathrm{NhF}/\varepsilon_0)[\alpha_{\mathrm{av}} + \mathrm{F}\mu^2/(3\mathrm{k_B T})] \tag{3}$$

$$N = N_A/V_m = \text{number density (number of molecules per volume unit)} \qquad (4)$$

$N_A = 6.02205 \times 10^{23}\,\text{mol}^{-1}$ Avogadro constant
V_m = molar volume
$h = 3\varepsilon/\ 2\varepsilon + 1$ correction factor considering the internal field
$F = (1 - f\alpha_{av})^{-1}$ correction factor for the reactive field
$f = (\varepsilon - 1)\ [2\pi\varepsilon_0\ a^3\ (2\varepsilon + 1)]^{-1}$
α_{av} = average polarizability of a molecule
$\varepsilon_0 = 8.854 \times 10^{-12}\ J^{-1}\ C^2\ m^{-1}$ dielectric constant of vacuum
μ = electric dipole moment
a = radius of the spherical cavity

For calculating a, we use Onsager's approximation: $4/3\pi\ N\ a^3 = 1$.

Maier and Meier [17] derived formulas for the dielectric constants of nematics:

$$\varepsilon_{\|} = 1 + (NhF/\varepsilon_0)[\alpha_{av} + 2/3\Delta\alpha\overline{P_2} + F(\mu^2/3k_BT)(1 - \{1 - 3\cos^2\beta\}\overline{P_2})] \qquad (5)$$

$$\varepsilon_{\perp} = 1 + (NhF/\varepsilon_0)[\alpha_{av} - 1/3\Delta\alpha\overline{P_2} + F(\mu^2/3k_BT)(1 + 1/2\{1 - 3\cos^2\beta\}\overline{P_2})] \qquad (6)$$

$\Delta\alpha = \alpha_{\|} - \alpha_{\perp}$
$\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$
$\overline{P_2}$ = order parameter
β = angle between molecule long axis and dipole moment
$\Delta\alpha$ = anisotropy of polarizability

The quantities α_{av}, $\Delta\alpha$, μ and β have been calculated using quantum chemical methods (CAChe/PM5). The molar volume V_m needed for calculation of the number density N is obtained by the group contribution method of Fedors [18].

We derived the empirical relation

$$\overline{P_2} = 0.363 \log T_{NI} \qquad (7)$$

between clearing temperature T_{NI} (°C) and $\overline{P_2}$ at room temperature (25°C) [20]. The refractive indices have been calculated by setting $\mu = 0$ in Eqs. (3, 5, 6) and by using the approximation

$$\varepsilon = n^2 \qquad (8)$$

From blends with mixture A we extrapolated T_{NI} and the anisotropic properties Δn and $\Delta\varepsilon$. The data are shown in Tables 4 and 5. Table 6 presents the data of the subjected compounds, calculated by quantum chemistry resp. Fedors' method. Using these data we can calculate the optical and dielectric constants, but in addition we need the knowledge of the order parameter $\overline{P_2}$. We do not have direct measurements of $\overline{P_2}$ for the mixtures including said compounds. But using Eq. (7) it is possible to calculate $\overline{P_2}$ at 25°C. This procedure causes difficulties because for most of the compounds we have directly determined clearing temperatures of single materials. On the other hand, we have extrapolated clearing temperatures from the blends with the Mixture A. Finally, it turns out that using both of the corresponding $\overline{P_2}$ the calculated Δn are very different from the extrapolated data.

This is shown in the cases of compounds P-3 (Table 7) and compound R-4 (Table 8). In both cases the calculated Δn are much higher than the extrapolated values. In order to reproduce the experimental values by calculation we must use quite low order parameters, which are much lower than calculated $\overline{P_2}$ of the Mixture A ($T_{NI} = 72.4$°C, $\overline{P_2}_{calc.} = 0.674$). This behaviour proves that the compounds P-3 and R-4 are not well compatible with the basic mixture. This is reflected also in the extrapolated $\Delta\varepsilon$, which are quite different from the data calculated using the order parameter optimised for Δn. The calculated data are more positive than the extrapolated values. Specially, in compound R-4 it is clear from the molecular structure,

TABLE 4 Extrapolated NI Temperature and Properties of Tetrahydropyrans

	Extrapolated from mixture A (15 wt%)		
	T_{NI} (°C)	Δn	$\Delta\varepsilon$
P-1	17.7	0.017	0.30
P-2	37.7	0.044	−0.40
P-3	31.0	0.024	−0.80
P-4	51.0	0.044	0.30
P-5	174.4	0.070	1.40
P-6	141.0	0.044	−1.70
P-7	196.4	0.097	2.10
P-8	182.4	0.084	1.40
P-9	175.0	0.077	0.30
P-10	164.4	0.064	0.30
P-11	137.7	0.124	4.73
P-12	105.7	0.097	3.40

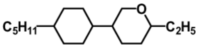
TABLE 5 Extrapolated NI Temperature and Properties of Bicyclohexanes

	Extrapolated from mixture A (15 wt%)		
	T_{NI} (°C)	Δn	$\Delta\varepsilon$
R-1	20.4	0.010	−1.3
R-2	37.0	0.010	−1.3
R-3	50.4	0.037	−0.6
R-4	51.0	0.024	0.3
R-5	61.0	0.044	−1.7
R-6	19.7	0.017	−0.3
R-7	12.4	0.010	−1.7
R-8	25.0	−0.030	0.1
R-9	149.7	0.117	2.3
R-10	133.7	0.092	2.5
R-11	198.7	0.090	3.0
R-12	189.7	0.087	−1.0

TABLE 6 Data Calculated for R4, P-3, R-12, P-9 and P-10

	μ (D)	$1–3\cos^2\beta$	α_{is} (a. u.)	$\Delta\alpha$ (a. u.)	V_m (cm^3/mol)
R-4	0.0140	0.4206	170.69	46.48	304.4
P-3	1.7163	0.7190	168.13	56.11	292.0
R-12	0.0134	0.2750	205.83	63.52	350.5
P-9	1.7268	0.5370	203.30	72.70	338.2
P-10	1.5935	0.0718	203.65	70.08	338.2

TABLE 7 Compound P-3

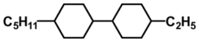


Comparison of Calculated and Extrapolated Data

$\overline{P_2}$	0.5414	0.6025	0.2200	Extrapol. from mixture A
T_{NI} (°C)	31[a]	45.7[b]	4.2[c]	31
$\varepsilon_{\parallel}$	2.838	2.8012	3.032	−0.8
$\varepsilon\perp$	3.321	3.3387	3.229	
$\Delta\varepsilon$	−0.483	−0.5375	−0.197	
$\varepsilon_{\parallel}$ ($\mu = 0$)		2.0381	1.9602	0.024
$\varepsilon_{\perp}(\mu = 0)$		1.8541	1.8930	
Δn		0.0660	0.0242	

[a] Clearing temperature extrapolated from the blend with mixture A.
[b] Clearing temperature of the pure compound.
[c] Calculated according to Eq. (7).

TABLE 8 Compound R-4



Comparison of Calculated and Extrapolated Data

$\overline{P_2}$	0.6848	0.6198	0.300	Extrapol. from mixture A
T_{NI} (°C)	77^b	51^a	6.8^c	51
$\varepsilon_{\|\|}$	1.8919	1.8825	1.8365	
$\varepsilon\perp$	1.7440	1.7487	1.7717	
$\Delta\varepsilon$	0.1479	0.1339	0.0648	−1
$\varepsilon_{\|\|}$ $(\mu=0)$	1.8919	1.8825	1.8364	
$\varepsilon_{\perp}(\mu=0)$	1.7439	1.7486	1.7716	
Δn	0.0549	0.0497	0.0241	0.024

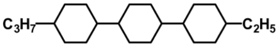
Annotations see Table 7.

that the $\Delta\varepsilon$ should be positive. By shifting the order parameter in Eqs. (5) and (6) we never can calculate negative $\Delta\varepsilon$ values for this compound. But when we assume that in addition to the dilution of Mixture A by adding R-4 $\Delta\varepsilon$ of the basic mixture is diminished, and negative $\Delta\varepsilon$ may be extrapolated. This explanation should be valid also for all compounds R-1 to R-8.

In the case of three ring compounds R-9 and R-10, the extrapolated $\Delta\varepsilon$'s are positive and thus 'normal', because the order parameters of three-ring compounds are similar to that of the basic mixture (see Table 5).

Tables 9 to 11 show the data calculated for compounds R-12, P-9 and P-10. For the cyclohexane derivative compound R-12 the order

TABLE 9 Compound R-12

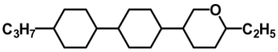


Comparison of Calculated and Extrapolated Data

$\overline{P_2}$	0.8504	0.8269	0.920	Extrapol. from mixture A
T_{NI} (°C)	220.1^b	189.7^a		189.7
$\varepsilon_{\|\|}$	1.988	1.984	2.000	
$\varepsilon\perp$	1.768	1.770	1.762	
$\Delta\varepsilon$	0.221	0.215	0.239	
$\varepsilon_{\|\|}$ $(\mu=0)$	1.8919	1.8825	2.0005	
$\varepsilon_{\perp}(\mu=0)$	1.7439	1.7486	1.7616	
Δn	0.0549	0.0497	0.0871	0.087

Annotations see Table 7.

TABLE 10 Compound P-9



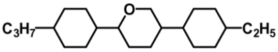
Comparison of Calculated and Extrapolated Data

$\overline{P_2}$	0.8142	0.685	Extrapol. from mixture A
T_{NI} (°C)	175^a	77.0	175
$\varepsilon_{\|}$	2.680	2.713	
$\varepsilon\perp$	2.986	2.970	
$\Delta\varepsilon$	−0.306	−0.257	
$\varepsilon_{\|}$ ($\mu = 0$)	2.0351	2.0084	
$\varepsilon_{\perp}(\mu = 0)$	1.7827	1.7961	
Δn	0.0914	0.0770	0.077

Annotations see Table 7.

parameter corresponding to the Δn is higher than those corresponding to the measured and extrapolated clearing temperatures. In the tetrahydropyran derivatives P-9 and P-10 it is opposite concerning the measured clearing temperatures, but concerning the extrapolated clearing temperatures the value for compound P-10 is slightly larger, for compound P-9 substantially lower.

TABLE 11 Compound P-10



Comparison of Calculated and Extrapolated Data

$\overline{P_2}$	0.8347	0.8044	0.59	Extrapol. from mixture A
T_{NI} (°C)	199.3^a	164.4^b	42.3	164.4
$\varepsilon_{\|}$	2.865	2.859	2.823	
$\varepsilon\perp$	2.654	2.656	2.674	
$\Delta\varepsilon$	0.211	0.203	0.149	
$\varepsilon_{\|}$ ($\mu = 0$)	2.0352	2.0291	1.9864	
$\varepsilon_{\perp}(\mu = 0)$	1.7856	1.7886	1.8100	0.064
Δn	0.0903	0.0871	0.0640	

Annotations see Table 7.

TABLE 12 Extrapolated Viscosities of Tetrahydropyran Derivatives based on Mixtures A, B and C

	Extrapolated from mixture A (15%)		Extrapolated from mixture B			Extrapolated from mixture C		
	η_{lin}	η_{log}	η_{lin}	η_{log}	conc. (wt%)	$\gamma 1_{lin}$[a]	$\gamma 1_{log}$[a]	conc. (wt%)
P-1	−0.9	9.0	10.7	12.1	15	–	–	–
P-2	−9.7	6.1	−0.80	6.1	15	−96.7	21.8	20
P-3	3.3	10.5	10.2	11.7	15	36.8	67.8	20
P-4	−2.8	8.0	6.50	9.40	15	−13.3	45.5	20
P-5	34.3	35.1	42.6	60.0	15	–	–	–
P-6	36.5	37.9	36.8	46.6	10	–	–	–
P-7	40.2	43.1	30.0	33.5	10	265.0	301.0	20
P-8	–	–	–	–	–	215.0	226.0	15
P-9	45.5	51.9	72.2	228	10	268.9	315.0	10
P-10	35.5	36.6	–	–	–	195.1	200.0	10
P-11	35.1	36.1	–	–	–	242.6	264.0	20
P-12	39.8	42.5	–	–	–	203.1	209.0	20

[a] Measured by transient current method [21].

[b] Units of η and $\gamma 1$ are mPa·s.

4.3. Viscosity of the New Compounds

The viscosity of the target compounds usually is calculated using a linear relation between viscosity and concentration:

$$\eta_{\text{blend}} = x_{\text{Mi}}\ \eta_{\text{Mi}} + x_{\text{t}}\eta_{\text{t}} \tag{9}$$

TABLE 13 Extrapolated Viscosities of Tetrahydropyran Derivatives based on Mixtures A, B and C

	Extrapolated. from mixture A (15%)		Extrapolated from mixture B (15%)		Extrpolated from mixture C (20%)	
	η_{lin}	η_{log}	η_{lin}	η_{log}	$\gamma 1_{lin}$[a]	$\gamma 1_{log}$[a]
R-1	−9.3	6.2	–	–	–	–
R-2	−19.1	3.9	−9.0	3.5	−208.1	6.4
R-3	−25	2.9	−18.0	1.9	−199.9	7.0
R-4	−11	5.7	−4.3	4.8	−120.0	16.9
R-5	−16	4.5	−8.6	3.6	−99.1	20.8
R-6	−1.7	8.7	–	–	−82.5	24.4
R-7	−3.5	8.0	−1.4	5.6	−78.2	25.4
R-8	1.2	9.6	6.0	9.2	−18.7	43
R-9	25.9	25.1	11.0	12.3	122.9	125.2
R-10	21	21.7	18.3	18.3	–	–

[a] Measured by transient current method [21].

[b] Units of η and $\gamma 1$ are mPa·s.

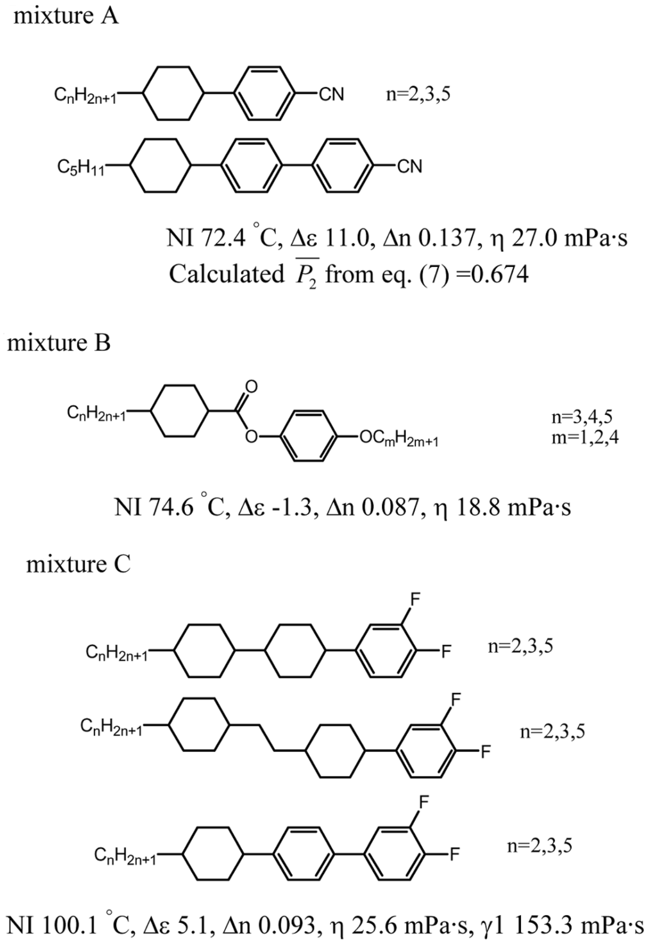


FIGURE 3 Base mixtures.

x_{Mi}, η_{Mi} = concentration and viscosity of the basis mixture
x_t,η_t = concentration and viscosity of the target compound
η_{blend} = viscosity of the blend of basis mixture and target compound

Equation (9) yields negative values for η_t, when the target compound has viscosity reducing effect of the total mixture and the deviation is larger. Kneppe *et al.* recommended a logarithmic dependence of the viscosity from the concentration for calculation of viscosities of mixtures, Eqs. (10) [19]. Equation (10) is better founded than Eq. (9) from the theoretical standpoint, but Eq. (9) is easier to handle in the practice.

$$\log \eta_{\mathrm{blend}} = x_{\mathrm{Mi}} \log \eta_{\mathrm{Mi}} + x_{\mathrm{t}} \log \eta_{\mathrm{t}} \tag{10}$$

In Tables 12 and 13 we have compiled the linearly and logarithmically extrapolated viscosities of subjected compounds from three types of base mixture (Figure 3). Most of the two-ring compounds possess negative viscosities by linear extrapolation. Comparing the data extrapolated from the polar mixture A and those from the low polar mixture B, we find that the data from the polar mixture are lower than the latter. However, when we compare the logarithmically extrapolated data, there is no substantial difference. Especially, all logarithmically extrapolated viscosities for two-ring compounds are positive with reasonable values.

The three-ring compounds generally possess higher viscosities, and in most cases there is no large difference between linear and logarithmic extrapolation. Irrespective of the mathematical treatment of the experimental data we can notice that the low polar compounds listed in Tables 4 and 5 possess low viscosities, which make the materials interesting for mixtures with faster response times suitable for applications in displays.

5. CONCLUSIONS

We have synthesized new derivatives of tetrahydropyran and cyclohexane with two and three rings. Due to their elongated molecular shape most of the compounds exhibit liquid crystalline phases, especially nematic phases. The differences in the clearing temperatures of the tetrahydropyran and cyclohexane derivatives can be explained by different amounts of most elongated conformers. Due to their small melting enthalpies the tetrahydropyran derivatives show large solubility in liquid crystal mixtures. We have compared calculated and measured $\Delta\varepsilon$ and Δn and found that the two-ring compounds have quite low order parameters when they are solved in basic mixtures. Especially the two-ring compounds possess unusually small viscosities. The new materials are useful components in mixtures for practical application.

REFERENCES

[1] Pauluth, D. & Tarumi, K. (2005). *J. SID*, *13*, 693.

[2] Demus, D. & Inukai, T. (2003). *Mol. Cryst. Liq. Cryst.*, *400*, 39.

[3] Vill, V. (2008). Liquid Crystal Database LiqCryst 4.7.

[4] Heckmeier, M., Plach, H., Ichinose, H., Nakajima, S., Sugiyama, Y. & Takashima, A. (2001). (Merck KGaA): DE 10116400.

[5] Koorishima, T., Takei, R., & Aoyama, E. (1985). (Asahi Glass Corp.): JP60-018571.

[6] Poetsch, E. & Reiffenrath, V. (1988). (Merck KGaA): DE 3632410.

[7] Osman, M. A. (1985). *Mol. Cryst. Liq. Cryst.*, *131*, 353.

[8] Schadt, M., Buchecker, R., & Villiger, A. (1990). *Liq. Cryst.*, *7*, 519.

[9] Buchecker, R. & Schadt, M. (1989). (F. Hoffmann-La Roche, Ltd.): EP315050.

[10] Scheuble, B., Weber, G., Kawamoto, K., Eidenschink, R., & Hittich, R. (1985). (Merck KGaA): EP158252; (b) Eidenschink, R., Gray, G. W., Toyne, K. J., & Wächtler, A. E. F. (1988). *Mol. Cryst. Liq. Cryst. Lett.*, *5*, 177.

[11] Takeuchi, K., Takatsu, H., Takehara, S., & Oosawa, M. (1993). (Dainippon Ink Corp.): JP 05-148483.

[12] Sugimori, S., Kojima, T., & Tsuji, M. (1982). (Chisso Corp.): EP 62470.

[13] Matsui, S., Miyazawa, K., Kato, T., & Sekiguchi, Y. (1997). (Chisso Corp.): JP09–110734.

[14] CAChe 6.1 Fujitsu Ltd. 2003.

[15] For the program calculating the Boltzmann distribution we are indebted to Dr. T. Inukai, former with Chisso Corporation Tokyo, Japan.

[16] Bahadur, B. (1992). *Liquid Crystals. Applications and Uses*, World Scientific: Singapore, 3, 68.

[17] Maier, W. & Meier, G. (1961). *Z. Naturforsch.*, *16a*, 262.

[18] Fedors, R. F. (1974). *Polymer Engineer. Sci.*, *14*, 147.

[19] Kneppe, H. & Schneider, F. (1986). *Fliessverhalten von Stoffen und Stoffgemischen*, Huethig und Wepf: Basel, 318.

[20] Demus, D. & Inukai, T. (2003). *Mol. Cryst. Liq. Cryst.*, *400*, 59.

[21] Imai, M., Naito, H., Okuda, M., & Sugimura, A. (1994). *Jpn. J. Appl. Phys.*, *33*, L 110.