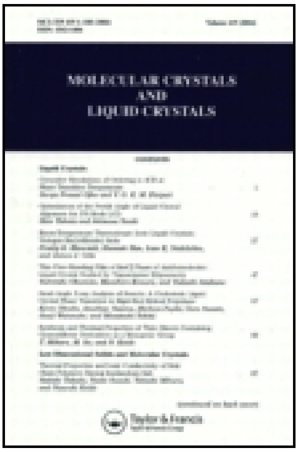


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Physical Properties of Novel Fluorinated Ethers and Ether Mixtures for Actively-Addressed, Twisted Nematic Liquid Crystal Displays

H. Takatsu [a] , K. Takeuchi [a] , M. Sasaki [a] , H. Ohnishi [a] & M. Schadt [b]

[a] Dainippon Ink & Chemicals, Inc., Rodic Co., Ltd., Ina-machi, Kitaadachi-gun, Saitama, 362, Japan

[b] Central Research Units, F. Hoffmann-La Roche Ltd., 4002, Basel, Switzerland

Version of record first published: 24 Sep 2006.

To cite this article: H. Takatsu , K. Takeuchi , M. Sasaki , H. Ohnishi & M. Schadt (1991): Physical Properties of Novel Fluorinated Ethers and Ether Mixtures for Actively-Addressed, Twisted Nematic Liquid Crystal Displays, Molecular Crystals and Liquid Crystals, 206:1, 159-177

To link to this article: http://dx.doi.org/10.1080/00268949108037728

Mol. Cryst. Liq. Cryst., 1991, Vol. 206, pp. 159–177
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Physical Properties of Novel Fluorinated Ethers and Ether Mixtures for Actively-Addressed, Twisted Nematic Liquid Crystal Displays

H. TAKATSU, K. TAKEUCHI, M. SASAKI and H. OHNISHI†

Dainippon Ink & Chemicals, Inc., †Rodic Co., Ltd., Ina-machi, Kitaadachi-gun, Saitama 362, Japan

and

M. SCHADT

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

(Received December 28, 1990; in final form April 12, 1991)

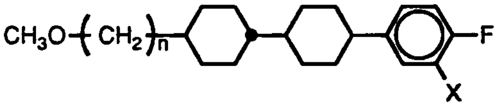
Several new classes of low polar, low viscous and optically weak anisotropic two- and three-ring fluorinated liquid crystals (LCs) with ether terminal groups are presented. Their material properties are investigated and compared with those of fluorinated LCs with alkenyl terminal groups. The 4-fluorophenylbicyclohexane ethers were found to exhibit dielectric anisotropies $\Delta\varepsilon$ which are similar to those of the corresponding alkenyls with 1-propenyl and 3-pentenyl group, whereas the alkenyls with 4-pentenyl group exhibit considerably lower $\Delta\varepsilon$-values. The optical and dielectric anisotropies of difluoroethers with odd numbers n of the methylene groups separating the ether oxygen from the rigid cores of the molecules are comparable, whereas compounds with odd n's were found to exhibit lower viscoelastic ratios γ_1/κ and therefore shorter response times in twisted nematic liquid crystal displays (TN-LCDs) than their even counterparts.

In mixtures designed for thin film transistor (TFT)-addressed TN-LCDs the new compounds are shown to exhibit very large voltage holding ratios HR $> 98\%$ which are maintained after extended exposure to high temperatures (80°C) and/or high light intensities.

1. INTRODUCTION

In general liquid crystal molecules consist of a central rigid core and of two terminal groups, with one of them frequently being a flexible terminal group. Not only the core but also the terminal groups strongly affect the mesomorphic and other physical properties of liquid crystals. This was shown by Schadt *et al.*$^{1-5}$ in a number of liquid crystals with alkenyl double bonds in their terminal groups. The authors show that double bonds and their position in the terminal group drastically affect the physical properties of liquid crystals, especially the elastic constants, but also their dielectric, optical and viscous performance.

To further investigate the effects non-alkyl terminal groups on the physical properties of liquid crystals we made a number of new, halogenated liquid crystals with ether terminal groups of the type;



In the following it will be shown to what extent the ether oxygen atoms affect the elastic, dielectric, optical and viscous properties of the liquid crystals. These properties shall be related to the electoro-optical performance of the new compounds in twisted nematic (TN) liquid crystal displays (LCDs). Moreover, we will show that the new materials exhibit a strongly reduced tendency to dissolve ionic impurities from the boundary aligning layers of TN-LCDs.[6] Thus, the new series of mono- and difluoro-ethers are especially suitable for application in actively-addressed TN-LCDs where large and stable specific resistivities are required.

2. RESULTS AND DISCUSSION

2.1 Comparison of Fluoro-Ethers with Fluoro-Alkenyls

Figure 1 shows the phase transition temperatures versus the number *n* of the methylene groups linking the oxygen in the ether terminal group with the rigid cores of the novel 4-fluorophenyl bicyclohexanes. Their nematic-isotropic (N-I) transition temperatures exhibit an odd-even effect versus *n*, with $T_{N\text{-}I}$ (odd) > $T_{N\text{-}I}$ (even). Moreover, a tendency to form smectic phase exists (Figure 1).

Figure 2 shows the phase transition temperatures of the novel 3,4-difluorophenyl bicyclohexanes. In analogy to their mono-fluoro counterparts of Figure 1, also the difluoro-ethers exhibit a pronounced odd-even effect of T_{NI} versus *n* (Figure 2). However, their tendency to form smectic phases is strongly reduced. This is shown by the odd mono-fluoro representatives in Figure 1 which exhibit enantiotropic smectic phases, whereas their odd difluoro-counterparts in Figure 2 are monotropically smectic. Figure 2 also shows about 30°C lower melting temperatures Tm for the difluoro-compounds.

To compare the material properties of the new mono- and difluorinated-ethers (upper part of Table I) with those of the corresponding fluorinated-alkenyl liquid crystals recently presented by Schadt *et al.*[5] (middle of Table I), the binary mixtures M1–M4 were prepared (Table I). Their composition is analogous to the aklenyl binaries M11–M14 (Table I). Each binary mixture consists of twenty mole per cent of the respective fluorinated compound and of 80% of the non-polar, low viscous, two-ring alkenyl liquid crystal 3CPOd$_3$1.[4,5] Table I shows the phase transition temperatures of the binary mixtures. Also shown in Table I are the static dielectric anisotropies $\Delta\varepsilon = (\varepsilon\|| - \varepsilon\perp)$ of the single LC-components determined at their respective reduced temperatures ($T_{N\text{-}I}$ − 10°C), where $T_{N\text{-}I}$ = nematic-isotropic transition temperature.

Table II lists the splay (k_{11}), twist (k_{22}) and bend (k_{33}) elastic constants of the

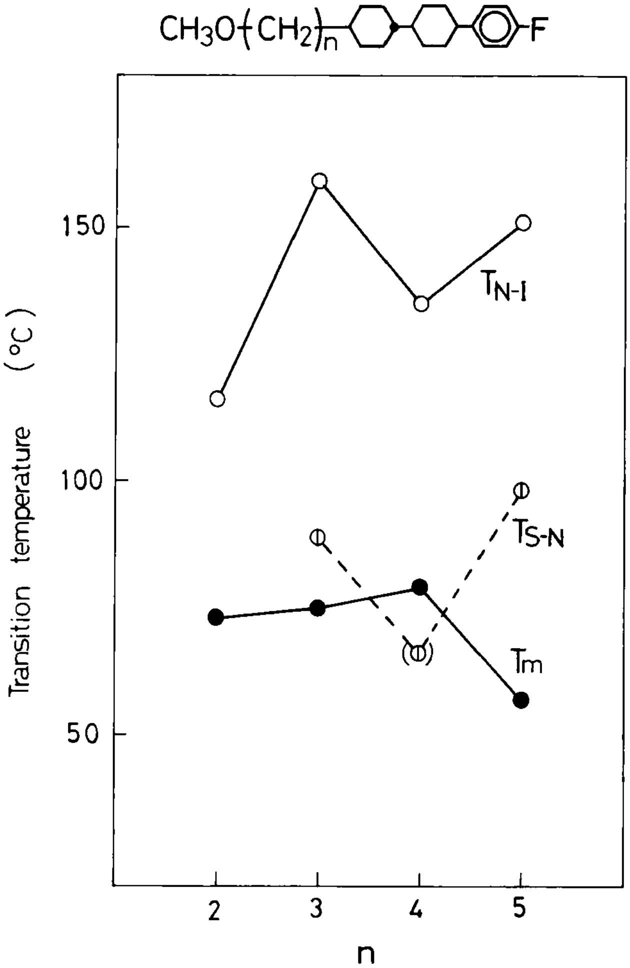


FIGURE 1 Phase transition temperatures against number *n* of methylene groups of 4-methoxyalkyl-4′-(4″-fluorophenyl)bicyclohexanes.

binary mixtures of Table I. Also listed in Table II is the elastic expression $\kappa = [k_{11} + (k_{33} - 2k_{22})/4]$ which—together with $\Delta\varepsilon$—determines the threshold voltage of TN-LCDs.[5] Included in Table II are $\varepsilon\perp$, the ordinary index of refraction n_o and the optical anisotropy $\Delta n = (n_e - n_o)$. The data in bold type were determined at the respective reduced temperatures ($T_{N\text{-}I}$ − 10°C), whereas the others are room temperature data (22°C). The temperature dependence of the elastic constants of the binary mixtures is shown in Figure 3.

The dielectric data of the monofluoro three-ring binary mixtures M3, M11, M13 and M14 of Table II suggest that the dielectric anisotropy ($\Delta\varepsilon$) of the pure 1O3CCPF with methoxypropyl ether and monofluoro group is about 10% larger than $\Delta\varepsilon$ of the pure monofluoro-alkenyls $1d_1$CCPF and $1d_3$CCPF (with odd double bond positions). Whereas, compared with the even-positioned 4-alkenyl $0d_4$CCPF, $\Delta\varepsilon$ of 1O3CCPF is about 75% larger. The low value of $\Delta\varepsilon$ of $0d_4$CCPF is due to the weak

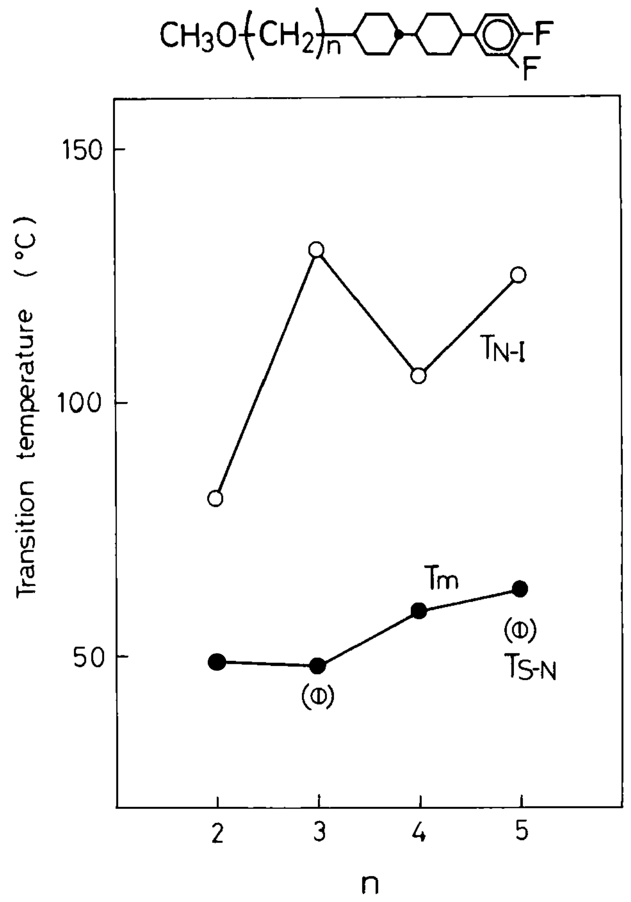


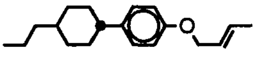
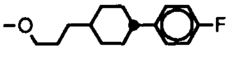
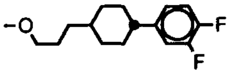
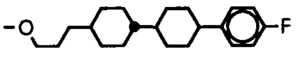
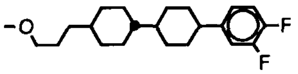
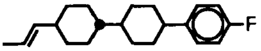
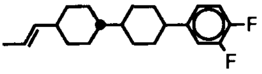
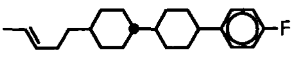
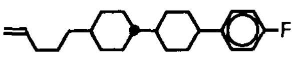
FIGURE 2 Phase transition temperatures against number *n* of methylene groups of 4-methoxyalkyl-4′-(3″,4″-difluorophenyl)bicyclohexanes.

contribution of even-positioned alkenyl double bonds to the induced polarization parallel to their long molecular axes.[1,5] This is an effect which is most pronounced in alkenyls with weak permanent dipole moments which do not camouflage the induced moments. However, it should be noted that care has to be taken when extrapolating dielectric anisotropies from binary mixtures to $\Delta\varepsilon$ of the pure compounds. Due to possibly different degrees of antiparallel molecular association in mixtures, rather large errors may occur. Indeed, the dielectric anisotropies determined directly in the single components (Table I) follows a slightly different order, namely $\Delta\varepsilon$ (0d$_4$CCPF) << $\Delta\varepsilon$ (103CCPF) < $\Delta\varepsilon$ (1d$_3$CCPF) < $\Delta\varepsilon$ (1d$_1$CCPF). Thus, the dielectric anisotropy of the monofluoro-ether 103CCPF is actually comparable to $\Delta\varepsilon$ of monofluoro-alkenyls with odd double-bond positions, whereas—due to the above—$\Delta\varepsilon$ (0d$_4$CCPF) is indeed considerably smaller. As expected from their weak aromatic structures the optical anisotropies of the novel ethers are comparably low as Δn of the alkenyls (Table II).

The elastic constants of the monofluoro, three-ring binary mixtures depicted in

TABLE I

Structures, nomenclature, phase transition temperatures and dielectric anisotropies of fluorinated cyclohexanes and bicyclohexanes with methoxypropyl- or alkenyl terminal groups. The binary mixtures Mi each comprise one fluorinated compound and the non-polar component 3CPOd$_3$1. The dielectric anisotropies Δε of the single components are determined at (T_{N-I} − 10°C)

NOMENCLATURE	STRUCTURE	T_m (°C)	T_{S-N} (°C)	T_{N-I} (°C)	Δε ($T_{N-I}-10$°C)
3CPOd$_3$1		42.4		57.5	−0.27
1O3CPF		27.0		-	-
1O3CP$_F$F		5.8		-	-
1O3CCPF		75	89	159	1.59
1O3CCP$_F$F		48	(42)	130	3.68
1d$_1$CCPF		105		194	1.75
1d$_1$CCP$_F$F		49	65	159	3.22
1d$_3$CCPF		83		175	1.65
0d$_4$CCPF		66		130	1.19
M1 = (**1O3CPF**, 3CPOd$_3$1)	(20 : 80 Mol%)	28		43.4	
M2 = (**1O3CP$_F$F**, 3CPOd$_3$1)	(20 : 80 Mol%)	28		36.4	
M3 = (**1O3CCPF**, 3CPOd$_3$1)	(20 : 80 Mol%)	25		73.6	
M4= (**1O3CCP$_F$F**, 3CPOd$_3$1)	(20 : 80 Mol%)	25		67.5	
M11 = (**1d$_1$CCPF**, 3CPOd$_3$1)	(20 : 80 Mol%)	32		75.0	
M16 = (**1d$_1$CCP$_F$F**, 3CPOd$_3$1)	(20 : 80 Mol%)	25		68.9	
M13 = (**1d$_3$CCPF**, 3CPOd$_3$1)	(20 : 80 Mol%)	22		77.7	
M14 = (**0d$_4$CCPF**, 3CPOd$_3$1)	(20 : 80 Mol%)	22		69.5	

M11, M13, M16 and M14 reference mixtures publ. in Liq. Cryst. 7, 519 (1990)

TABLE II

Elastic, dielectric and optical properties of the reference compound 3CPOd$_3$1 and of the fluorinated binary ether- and alkenyl mixtures Mi. The data in bold type were determined at ($T_{N\text{-}I}$ − 10°C), the others are 22°C data

LIQUID CRYSTAL	$k_{11}/10^{-12}$N	$k_{22}/10^{-12}$N	k_{33}/k_{11}	$\kappa/10^{-12}$N	$\varepsilon_\perp$	$\Delta\varepsilon$	n_0	Δn
3CPOd$_3$1 (100%)	**8.82**	**4.55**	**1.16**	**9.1**	**3.07**	**−0.268**	**1.486**	**0.089**
M1 = (**1O3CPF**, 3CPOd$_3$1)	**8.29**	**4.48**	**1.18**	**8.5**	**3.41**	**0.330**	**1.489**	**0.085**
20 80	11.3*	5.10*	1.22*	12.2*	3.45*	0.400*	1.491	0.096
M2 = (1O3CP$_F$F, 3CPOd$_3$1)	**8.42**	**4.05**	**1.11**	**8.8**	**3.80**	**0.812**	**1.490**	**0.086**
20 80	9.85*	4.56*	1.12*	10.3*	3.80*	0.905*	1.490	0.091
M3 = (1O3CCPF, 3CPOd$_3$1)	**7.66**	**4.28**	**1.16**	**7.8**	**3.27**	**0.388**	**1.482**	**0.078**
20 80	17.4*	6.98*	1.22*	19.2*	3.46	0.561	1.491	0.106
M4 = (1O3CCP$_F$F, 3CPOd$_3$1)	**7.82**	**4.08**	**1.09**	**7.9**	**3.51**	**0.807**	**1.484**	**0.080**
20 80	16.9*	6.95*	1.11*	18.0*	3.69	1.208	1.490	0.104
M11 = (**1d$_1$CCPF**, 3CPOd$_3$1)	**8.31**	**4.10**	**1.22**	**8.8**	**2.99**	**0.359**	**1.482**	**0.083**
20 80	17.9	7.15	1.31	20.2	3.14	0.485	1.498	0.111
M16 = (**1d$_1$CCP$_F$F**, 3CPOd$_3$1)	**8.47**	**4.34**	**1.16**	**8.8**	**3.28**	**0.741**	**1.482**	**0.084**
20 80	18.4	7.07	1.20	20.4	3.42	1.068	1.491	0.109
M13 = (**1d$_3$CCPF**, 3CPOd$_3$1)	**7.74**	**3.82**	**1.25**	**8.2**	**2.95**	**0.353**	**1.482**	**0.080**
20 80	17.7	7.30	1.35	20.0	3.11	0.483	1.493	0.109
M14 = (**0d$_4$CCPF**, 3CPOd$_3$1)	**7.24**	**3.71**	**1.10**	**7.4**	**2.97**	**0.219**	**1.485**	**0.077**
20 80	15.9	6.51	1.10	16.9	3.11	0.284	1.492	0.103

* extrapolated

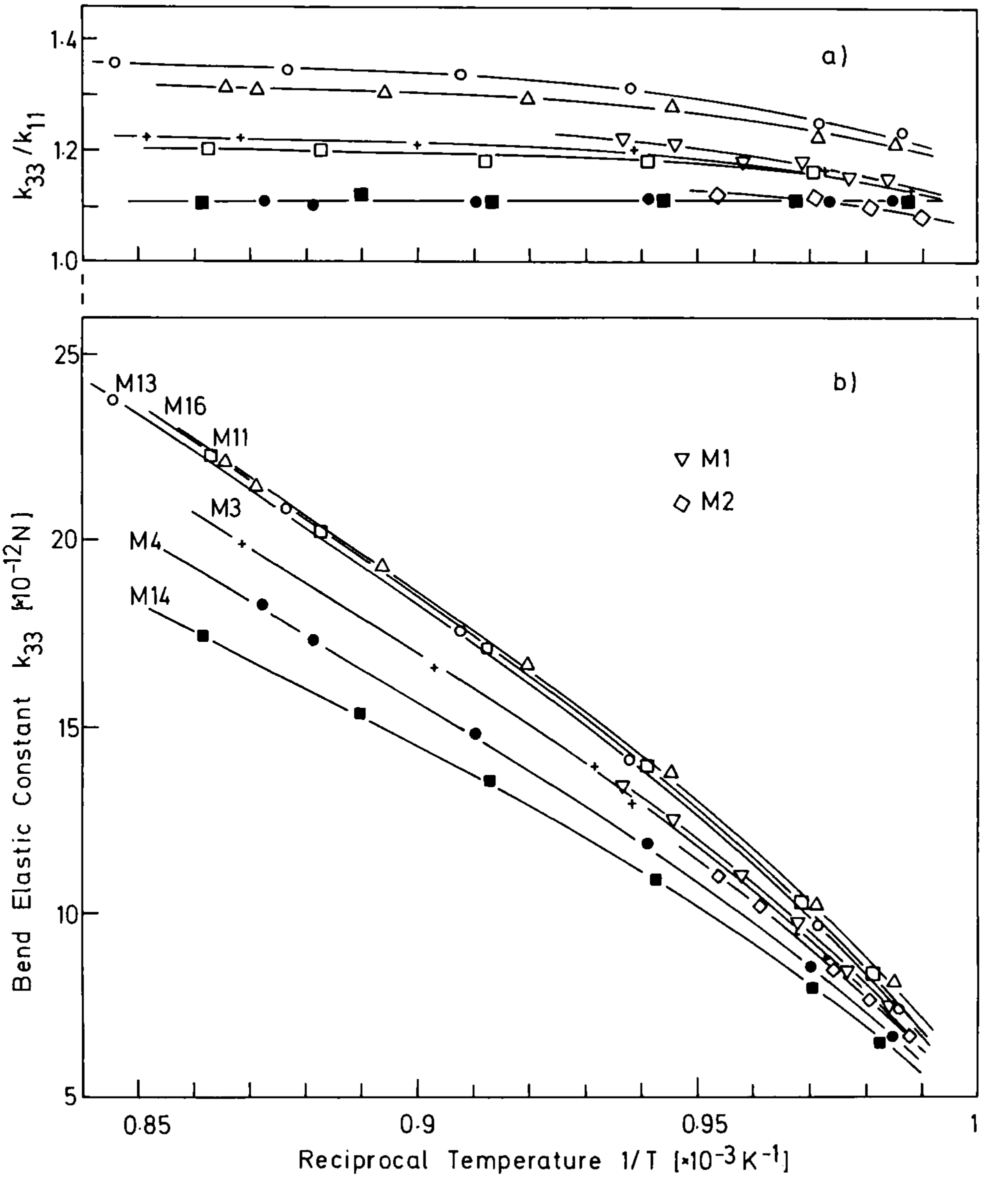


FIGURE 3 Temperature dependence of the bend elastic constant (k_{33}) and of the bend/splay elastic ratio (k_{33}/k_{11}) of fluorinated binary ether- and alkenyl-mixtures.

Figure 3 and Table II show that alkenyl $1d_1$CCPF induces the largest bend elastic constant k_{33} (cf. M3, M11, M13 and M14 in Table II). Except for $0d_4$CCPF, Table II leads to the lowest bend/splay elastic ratio k_{33}/k_{11} (= 1.6) for 103CCPF. These finding show that the elastic ratios k_{33}/k_{11} of the new monofluoro-ethers lie—like those of analogous compounds with saturated hydrocarbon terminal groups[1]—in between the large k_{33}/k_{11}—ratios of alkenyls with odd double bond positions and the low values of even-positioned alkenyls. As shown below this result is confirmed in mixtures comprising only ethers (Table IV).

Table III shows the bulk (η) and the rotational (γ_1) viscosities as well as the viscoelastic ratios γ_1/κ of the above binary mixtures. Also included in Table III are the respective data for the low viscous, non-polar, single-alkenyl component $3CPOd_31$.[5] The data in bold type were determined at ($T_{N\text{-}I}$ − 10°C), whereas the others are room temperature data (22°C). Also included in Table III are the threshold voltages V_{10} determined at 10% transmission of TN-LCDs with $d = 6$ μm cell gaps. The TN-LCD response times, which were determined at the respective driving voltages $V = 2.5 \times V_{10}$, correspond with the transmission changes t_{on} (0% → 90%) and t_{off} (100% → 10%). These changes are related to rather large changes of the nematic director deformation of the twisted nematic helix. The temperature dependencies of γ_1 and t_{off} for the binary mixtures are depicted in Figure 4.

Because the electro-optical measurements were made in $d = 6$ μm TN-LCDs, that is, close to the first TN-transmission minimum, the threshold voltages V_{10} in Table III should be slightly larger than the corresponding thresholds Vc for mechanical deformation of the TN-LCDs.[7] Indeed, from inserting the elastic and the dielectric constants κ and Δε from Table II into the equation governing the mechanical threshold voltage Vc of TN-LCDs[7]

$$Vc = \pi(\kappa/\varepsilon_o\Delta\varepsilon)1/2. \qquad (1)$$

it follows that the Vc-values are between 10% and 20% lower than the V_{10}-data in Table III. This shows that the elastic and the dielectric constants of Table II correspond well with the threshold voltage V_{10} in Table III.

Among the monofluoro-mixtures depicted in Table III, mixture M3, which comprises the ether 103CCPF, exhibits the lowest threshold. This is in agreement with its lowest κ/Δε-ratio (Table III). Among the difluoro-compounds, $103CCP_FF$ in M4 leads to the lowest threshold voltage. This again agrees with the rather large dielectric anisotropy Δε of M4 combined with its medium elastic expression κ.

From a small-angle approximation[8] one expects the turn-off times t_{off} of TN-LCDs to be proportionate to the visco-elastic ratio γ_1/κ. Qualitatively this indeed holds for the ether mixtures M1–M4 in Table III despite the large director deformation which the driving voltage $V = 2.5 \times V_{10}$ induces in our experiments. However, in case of the alkenyl mixtures M11–M14, t_{off} does not quite correlate with γ_1/κ; their turn-off times are shorter than expected from the corresponding viscoelastic ratios (Table III). This may be due to the large director deformation which could cause deviations from the small-angle approximation on which the proportionality $t_{off} \propto \gamma_1/\kappa$ is based.

2.2 Material Properties of Pure Fluoro-Ether Mixtures

To evaluate the potential of the new fluorinated ethers for practical applications requiring broad nematic phases and adequately low threshold voltages, a series of ternary mixtures were investigated which comprise the two-ring compound $103CP_FF$ as well as the three-ring components 103CCPF and $103CCP_FF$. Figure 5 shows the N-I transition temperatures of the ternary mixtures which exhibit nematic phases

TABLE III

Bulk (η) and rotational (γ_1) viscosities, visco-elastic ratio (γ_1/κ), dielectric anisotropy, TN-LCD threshold voltage V_{10} at 10% transmission, threshold voltage (*Vc*) for mechanical deformation of a TN-LCD and response times t_{on} and t_{off} of the binary mixtures Mi. The data in bold type were determined at ($T_{N\text{-}I}$ − 10°C), the others are 22°C data. TN-LCDs from Optrex, Japan, were used for the experiments; *Vc* was determined from κ and Δε in Table II using Equation (1)

LIQUID CRYSTAL	η/cP	γ_1/cP	$\gamma_1/\kappa/10^{-12}m^{-2}s^{-1}$	Δε	V_c/V	V_{10}/V	t_{on}/ms	t_{off}/ms
3CPOd$_3$1 (100%)	**4.7** 13.5	**25** 86	**2.7**	**–0.268**		–	–	–
M1 = (**1O3CPF**, 3CPOd$_3$1) 20 80	**7.1** 10.8*	**27.0** 56.0*	**3.2** 4.6*	**0.330** 0.400*	**5.4** 5.5*	**6.0** 6.7	**9.0** 10.9	**14.2** 16.2
M2 = (**1O3CP$_F$F**, 3CPOd$_3$1) 20 80	**9.9** 11.5*	**36.0** 48.5*	**4.1** 4.7*	**0.812** 0.905*	**3.5** 3.6*	**3.6** 3.8	**10.8** 11.7	**18.3** 19.2
M3 = (**1O3CCPF**, 3CPOd$_3$1) 20 80	**4.6** 16.8*	**12.5** 86.0*	**1.6** 4.5*	**0.388** 0.561	**4.8** 6.1	**5.0** 7.0	**4.8** 11.9	**8.5** 16.1
M4 = (**1O3CCP$_F$F**, 3CPOd$_3$1) 20 80	**5.1** 16.3	**18.7** 100	**2.4** 5.6	**0.807** 1.208	**3.3** 4.2	**3.5** 4.8	**5.3** 10.5	**11.0** 19.0
M11 = (**1d$_1$CCPF**, 3CPOd$_3$1) 20 80	**3.7** 15.2	**13.4** 86	**1.5** 4.3	**0.359** 0.485	**5.3** 6.9	**5.6** 8.0	**3.6** 10	**6.5** 13
M16 = (**1d$_1$CCP$_F$F**, 3CPOd$_3$1) 20 80	**4.6** 15.2*	**18.0** 95*	**2.0** 4.7*	**0.741** 1.068*	**3.6** 4.7	**3.9** 5.3	**4.2** 9	**8.4** 15
M13 = (**1d$_3$CCPF**, 3CPOd$_3$1) 20 80	**3.7** 14.8	**12.4** 115	**1.5** 5.8	**0.353** 0.483	**5.1** 6.8	**5.4** 8.1	**3.7** 10	**7.4** 14
M14 = (**0d$_4$CCPF**, 3CPOd$_3$1) 20 80	**4.8** 11.5*	**14.9** 85*	**2.0** 5.0*	**0.219** 0.284	**6.1** 8.2	**6.2** 9.2	**5.0** 12	**10.0** 17

* extrapolated

TABLE IV

Material and electro-optical properties of the difluoro ether mixtures M22 and M = (50% M21, 50% M22). The data in bold type are determined at ($T_{N\text{-}I}$ − 10°C), the others at T = 22°C = constant. TN-LCD response time $\tau = t_{on} = t_{off}$ in d = 6 μm cells

MIXTURE	$k_{11}/10^{-12}N$	$k_{22}/10^{-12}N$	k_{33}/k_{11}	$\kappa/10^{-12}N$	$\Delta\varepsilon$	Δn	η/cP	γ_1/cP	V_{10}/V	τ/ms
M22	**4.14**	**3.37**	**1.59**	**4.1**	**3.08**	**0.051**	**-**	**19.6**	**1.38**	**-**
	8.50	5.60	1.77	9.5	5.65	0.077	47.7	324	1.60	104
M = (M21, M22)	**4.55**	**3.40**	**1.48**	**4.5**	**3.182**	**0.054**	**-**	**13.5**	**1.51**	**-**
50 50	10.7	6.53	1.58	11.7	6.75	0.080	42.8	288	1.72	80

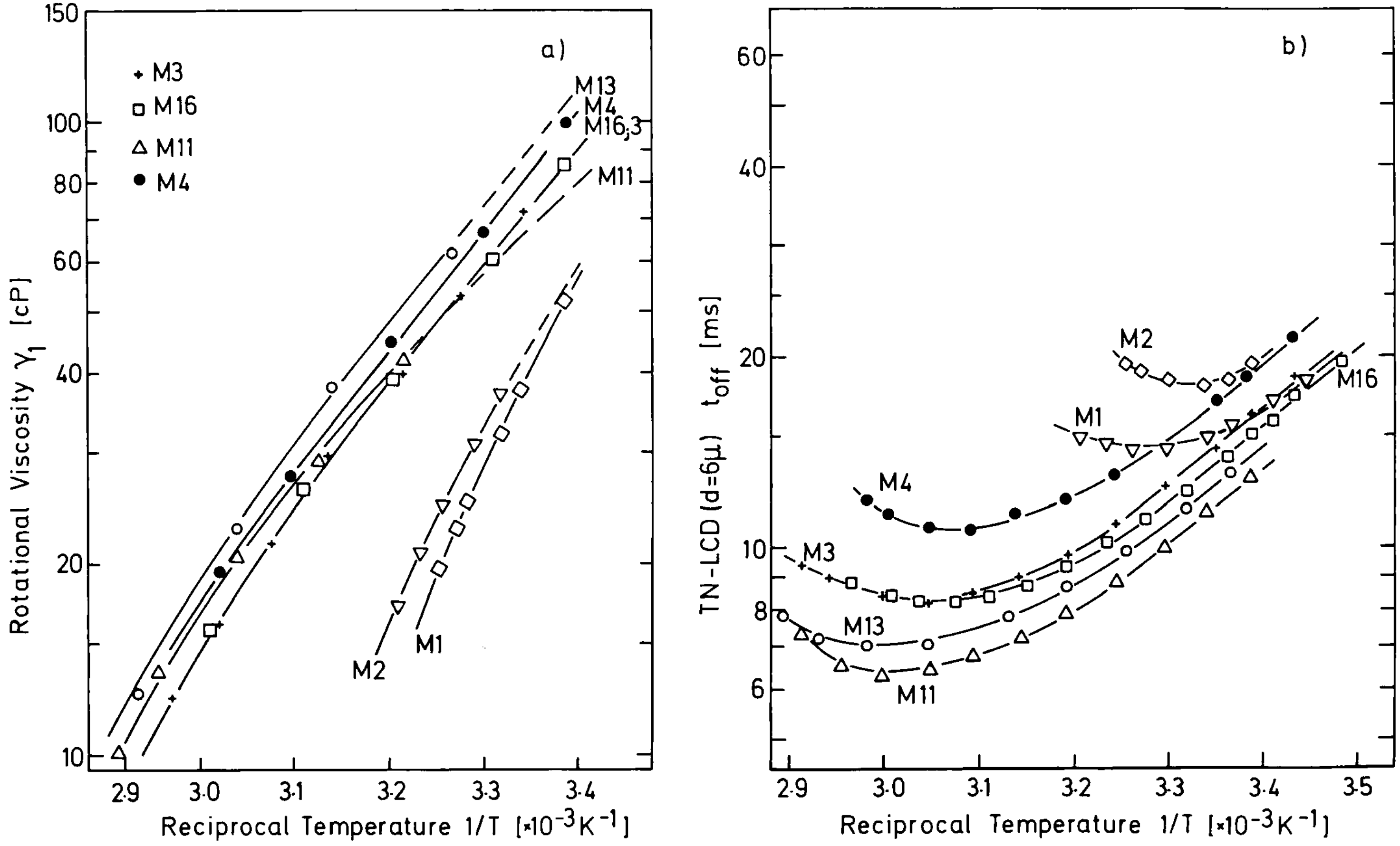


FIGURE 4 Temperature dependence of the rotational viscosity γ_1 and of the response time t_{off} of TN-LCDs comprising fluorinated binary mixtures with ether or alkenyl terminal groups.

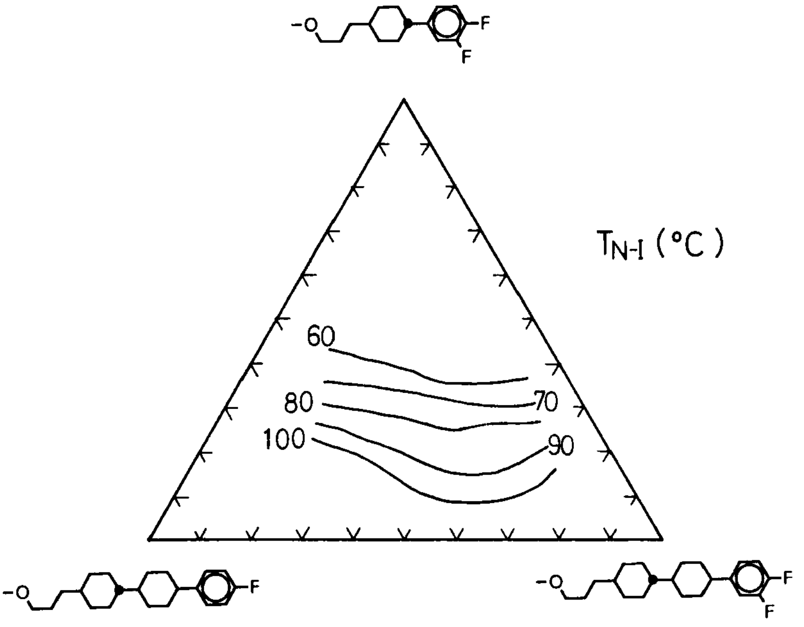


FIGURE 5 Nematic-isotropic (N-I) transition temperatures of ternary mixtures comprising fluorinated components with methoxypropyl groups.

at 20°C versus mixture composition. From Figure 5 it follows that broad nematic phases with melting temperatures below 20°C and N-I transitions as high as 90°C can be achieved with mixtures which comprise up to 80% three-ring ethers. This illustrates the excellent solubility of the new compounds and their pronounced tendency to depress crystallization.

Figure 6 shows the TN-LCD threshold voltages V_{10} of the same mixture as in Figure 5. Again, because of their low optical anisotropies Δn (22°C) = 0.077 the measurements were made in TN-LCDs operated in the first transmission minimum ($\Delta n \cdot d \simeq 0.5$; $d = 6$ μm). From Figure 6 it follows that threshold voltages $1.2 \leq V_{10} \leq 1.8$ volts can be achieved at room temperature. Despite its high $T_{NI} = 90°C$ the ternary mixture with the broadest temperature range still exhibits a rather low threshold voltage $V_{10} = 1.8$ volts (Figures 5 and 6).

To investigate the influence of odd and even numbers *n* of methylene groups in the terminal group of difluoro-ethers which separate the oxygen from the rigid core, the material properties of the two binary mixtures M21 and M22 as well as different blends among them were investigated. Both mixtures comprise three-ring difluoro-components. M21 consist of the odd homologues $103CCP_FF$ and $105CCP_FF$, whereas M22 contains the even homologues $102CCP_FF$ and $104CCP_FF$, both in molar proportions 50/50.

Figure 7 shows the phase transition temperatures of the quaternary ether mixtures upon blending the two binary mixtures M21 and M22 in different proportions. From Figure 7 it follows that smectic phases occur when increasing the total amount of odd ethers (M21) above 50%. Mixture M comprising 50 mole % of M21 and

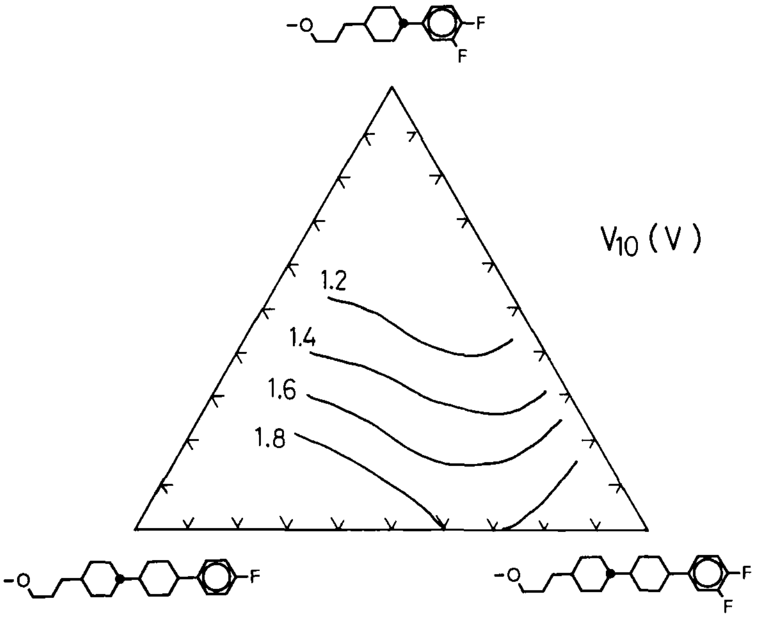


FIGURE 6 TN-LCD threshold voltage V_{10} of ternary mixtures comprising fluorinated methoxypropyl components. Measurements made at 22°C, TN-LCD cell gap d = 6 μm.

50 mole % of M22 exhibits a pronounced eutectic depression which leads to the large nematic phase of M (Figure 7).

Figure 8 shows the dependence of the elastic constants k_{11}, k_{33}, k_{33}/k_{11}, which were measured at 22°C, and of the elastic expression κ versus composition of the quaternary mixture (M21, M22). It is interesting to note in Figure 8 that k_{33}/k_{11} slightly decreases with increasing concentration of M21, *i.e.*, with increasing concentration of odd difluoro-ethers, whereas κ increases.

The dependences of the TN-LCD threshold voltage V_{10} and of the dielectric anisotropy $\Delta\varepsilon$—both determined at 22°C—versus the composition of mixture (M21, M22) are depicted in Figure 9. Figure 9 shows that $\Delta\varepsilon$ increases with increasing concentration of M21. Despite the increase of $\Delta\varepsilon$, V_{10} does not decrease with increasing M21 but slightly increases (Figure 9), the reason being the simultaneous strong increase of the elastic expression κ (Figure 8) which causes $\kappa/\Delta\varepsilon$ in Equation (1) to increase.

Table IV shows all relevant material properties as well as the TN-LCD threshold voltages V_{10} and the response times $\tau = t_{on} = t_{off}$ of mixtures M22 and M = (50% M21, 50% M22). The data in bold type were determined at the respective normalized temperatures ($T_{N\text{-}I}$ − 10°C), whereas the others are room temperature data (22°C). From the room temperature response times τ in Table IV it follows that τ increases with decreasing concentration of odd ethers (M21). Thus, τ (M22) is 30% larger than τ (M). Quantitatively, this increase corresponds with the increase of the visco-elastic ratio γ_1/κ which occurs upon increasing the concentration of even ethers (cf. γ_1 and γ_1/κ in Table IV). Moreover, from the ($T_{N\text{-}I}$ − 1)-data in Table IV it follows that both the dielectric and the optical anisotropy of odd and

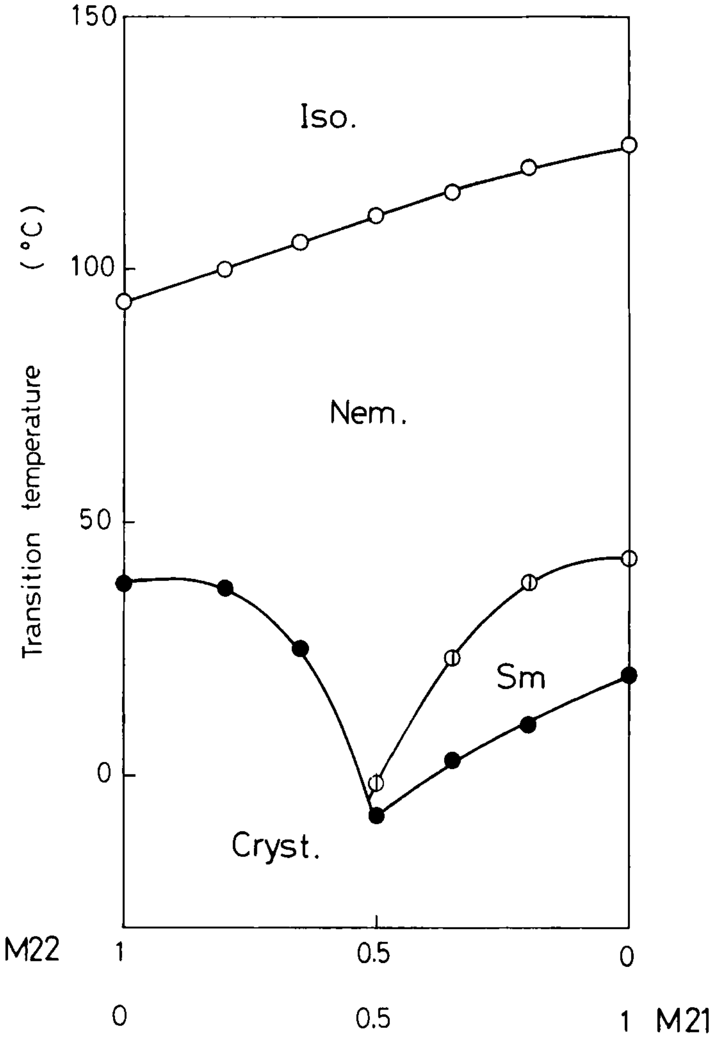


FIGURE 7 Phase transition temperatures of ternary mixture (M21, M22) for different molar proportions of M21 and M22. M21 consists of the odd homologues $103CCP_FF$ and $105CCP_FF$, whereas M22 contains the even homologues $102CCP_FF$ and $104CCP_FF$, both in molar proportions 50/50.

even difluoro-ethers are very similar, whereas the elastic constant ratio k_{33}/k_{11} slightly with an increasing proportion of odd ethers.

2.3 Application of Fluoro-Ethers in TFT-TN-LCDs

Based on above we designed four nematic mixtures for thin film transistor (TFT)-addressed TN-LCDs in which the favourable properties of fluorinated ethers and alkenyls are combined. The only polar components used in the four mixtures with different thresholds, are mono- and difluoro-ethers and alkenyls of the type depicted in Table I. Because of their strong solubility for residual ions trapped in the polyimide aligning layers of TN-LCDs, components with (strongly polar) cyano

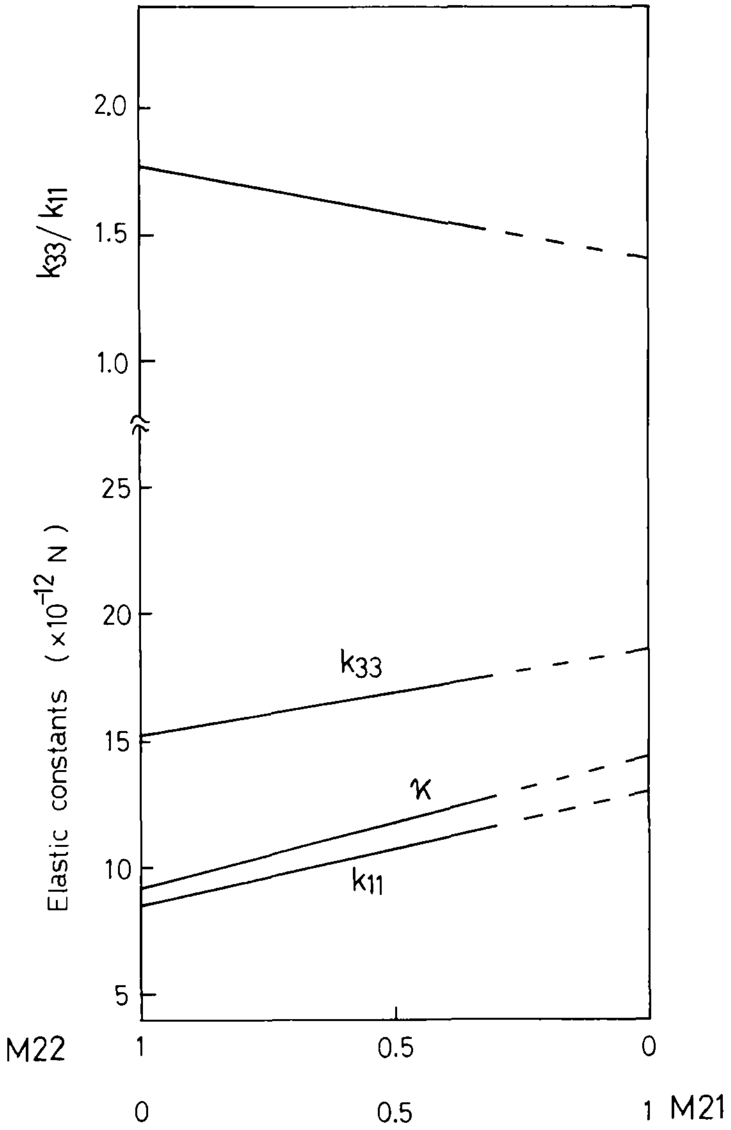


FIGURE 8 TN-LCD threshold voltage V_{10} at 10% transmission (cell gap d = 6 μm) and dielectric anisotropy Δε versus mixture composition (M21, M22). Measurements made at 22°C.

groups were avoided. Thus, we expect the four TFT-mixtures to exhibit (i) large initial bulk resistivities which are (ii) maintained in the LCDs. That is, discharging of the TFTs during the video frame time T = 40 ms by too short RC-times of the liquid crystal layer should be minimal for the new mixtures. R and C are the residual resistivity and the capacitance of a TN-LCD mixture element.

Table V shows some properties of the four novel TFT-mixtures. The abbreviations and measuring conditions are described in the table caption. From Table V it follows that low threshold voltage as well as broad nematic phases can be achieved

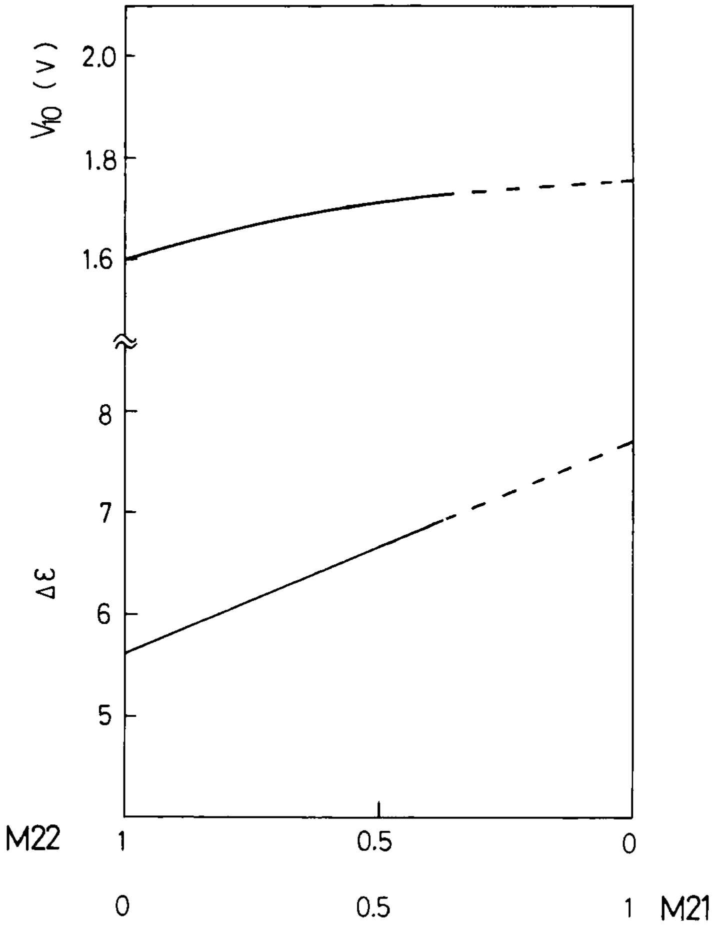


FIGURE 9 Bend (k_{33}), splay (k_{11}) elastic constants, elastic expression $\kappa = [k_{11} + (k_{33} - 2k_{22})/4]$ and elastic ratio k_{33}/k_{11} versus mixture composition (M21, M22) determined at 22°C.

by using the fluorinated liquid crystals only as polar components. From their large holding ratios HR (Table V) it follows that discharging of the pixel capacitance C of TFT-TN-LCDs comprising these mixtures does indeed hardly occur during the television frame time T. Thus, the image information read into pixels by the 64 μs gate-addressing pulse is maintained during T. This is shown by the large holding ratios HR in Table V which exceed 98% despite the threshold voltage as low as V_{10} = 1.5 volts and rather large dielectric anisotropies $\Delta\varepsilon$ = 8.3.

Figure 10 shows the stability of the holding ratio HR of TFT-mixture RDE-00629 (Table V) against exposure to high temperatures and high light intensities. The tests were performed in TN-LCDs exhibiting TFT-grade polyimide aligning layers. During the heating test the LCDs were exposed to 80°C. The light stability tests were made at 30°C under the 1.1 kW Xenon lamp of a Hanau Sun Tast apparatus with no protecting polarizers or UV-cut-off filters. The holding ratios HR were determined at room temperature. The heating tests shows that no deg-

TABLE V

Properties of fluorinated TFT-mixtures. T_{-N} = low temperature transition temperature into the nematic phase; $\tau = t_{on} = t_{off}$ = TN-LCD response time determined in $d = 6$ μm cells (addressing pulse width 64 μs, frame time $T = 40$ ms); HR = voltage holding ratio of a pixel during $T = 40$ ms. Measurements made at 22°C

	RDE-00458	RDE-00459	RDE-00460	RDE-00629
T_{N-I} (°C)	107	78	94	101
T_{-N} (°C)	−45	−50	−12	−55
Δn	0.084	0.079	0.082	0.081
$\Delta \varepsilon$	8.3	7.6	5.2	5.6
V_{10} (V)	1.7	1.5	2.1	1.9
$\eta_{20°C}$ (C.P.)	34	27	21	26
τ ($\tau_r = \tau_d$) (msec)	39	38	25	34
Voltage Holding Ratio(%)	98.9	98.9	99.0	99.5

radation of the large initial holding ratio HR = 99.3% occurs during high temperature exposure. That is, the large initial bulk resistivity of the TFT-mixture does not degrade. In the light stability test (Figure 10) an initial fast decrease of holding ratio from HR = 99.3% → HR = 98.7% occurs during the first hour of exposure; then virtually no further decrease occurs. From Figure 10 it follows that the new liquid crystals indeed perform well, even under severe environmental conditions.

3. CONCLUSIONS

The material properties of a number of new mono- and difluorinated nematic liquid crystals with ether terminal groups are correlated with their electro-optical performance in TN-LCDs. Their dielectric, elastic, optic, viscous and thermal properties are compared with those of fluorinated alkenyls and combined in mixtures for thin film transistor (TFT)-addressed TN-LCDs. The new compounds favourably combine low viscosity and broad nematic mesophases as well as a broad range of dielectric anisotropies with large specific resistivities and low solubilities for residual ions trapped in the polymer boundary aligning layers of LCDs. Consequently, large holding ratios for charge storage in TFT-TN-LCDs result which efficiently prevent discharging of the LCD-picture elements during the video frame time.

The bend/splay elastic ratios of new mono-fluorinated ethers lie in between the large k_{33}/k_{11}-ratios of alkenyls with odd double-bond positions and the low ratios of even-positioned alkenyls. Among the ether- and alkenyl-difluoro-compounds

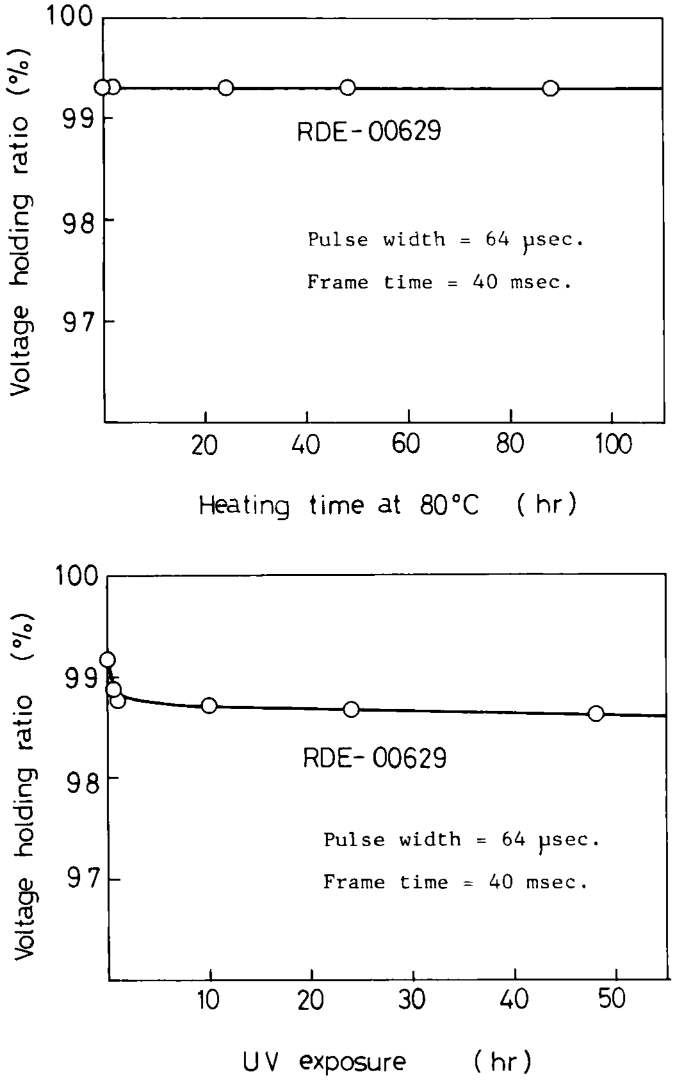


FIGURE 10 Heat and light stability of the voltage holding ratio HR of TN-LCDs comprising TFT-mixture RDE-00629.

investigated, the odd ether $103CCP_FF$ was found to exhibit the largest dielectric anisotropy. It is also the odd difluoro ethers which exhibit lower rotational viscosities γ_1 than their even counterparts, where odd and even refers to the number n of methylene groups liking the oxygen in the ether terminal group with the respective rigid core of the molecule. The low γ_1 values of the odd ethers result despite their terminal groups which are by one CH_2-group longer than those of their even counterparts. Thus, the oxygen position in the ether terminal groups of the new compounds does hardly affect k_{33}/k_{11}, whereas it slightly affects $\Delta\varepsilon$ and rather strongly the visco-elastic ratio γ_1/κ and therefore the electro-optical response times.

References

1. M. Schadt, M. Petrzilka, P. R. Gerber and A. Villiger, *Mol. Cryst. Liq. Cryst.*, **122**, 241 (1985).
2. M. Schadt, R. Buchecker, F. Leenhouts, A. Villiger and M. Petrzilka, *Mol. Cryst. Liq. Cryst.*, **139**, 1 (1985).
3. R. Buchecker and M. Schadt, *Mol. Cryst. Liq. Cryst.*, **149**, 359 (1987).
4. M. Schadt, R. Buchecker and K. Muller, *Mol. Cryst. Liq. Cryst.*, **5**, 293 (1989).
5. M. Schadt, R. Buchecker and A. Villiger, *Mol. Cryst. Liq. Cryst.*, **7**, 519 (1990).
6. H. Takatsu and K. Takeuchi, Japanese Patent Application, 1989-257316.
7. M. Schadt and P. Gerber, *Zeitschr. Naturforsch.*, **37a**, 165 (1982).
8. E. Jakeman and P. Raynes, *Phys. Lett.*, **39A**, 69 (1972).