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New Nematic Liquid Crystals: Influence of Rigid Cored, Alkenyl Side-Chains and Polarity on Material and Display Properties

M. Schadt [a] , R. Buchecker [a] , F. Leenhouts [a] , A. Boller [a] , A. Villiger [a] & M. Petrzilka [a]
[a] F. Hoffmann-La Roche and Co. Ltd, Central Research Units, Basek, CH-4002, Switzerland
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New Nematic Liquid Crystals: Influence of Rigid Cores, Alkenyl Side-Chains and Polarity on Material and Display Properties

M. SCHADT, R. BUCHECKER, F. LEENHOUTS, A. BOLLER, A. VILLIGER and M. PETRZILKA

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

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From the design of non-polar molecular structures exhibiting different rigid cores and isolated C=C double bonds in different side-chain positions and from investigations into the static dielectric birefringence, viscous, and all three elastic constants k_1, k_2, k_3, new, negative dielectric anisotropic nematic liquid crystals result, namely apolar alkenyls, which are shown to cover a wide range of material properties, including large twist constants k_2. The combination of double bonds in 4-position, with rigid cores comprising heterocyclic rings is shown to lead to exceptionally low elastic ratios $k_3/k_1 \sim 0.4$ with simultaneously low optical anisotropies and low rotational viscosities γ_1. Moreover, laterally substituted alkenyls are shown to exhibit large negative dielectric anisotropies rendering them applicable for low viscous, positive contrast guest-host mixtures with high order parameters $0.72 \leq S \leq 0.78$. The stability of the new nematics comprising isolated double bonds is shown to be comparable to that of saturated PCHs or biphenyls.

Keywords: LCD's, nematic liquid crystals, alkenyls, LC-material properties, material-structural relationships

1. INTRODUCTION

An essential requirement for further improving liquid crystal display (LCD) performance and for extending their applicability into new areas are improved liquid crystal materials. The design of LC-molecules having specific physical and electro-optical properties requires a better understanding of the correlations between molecular

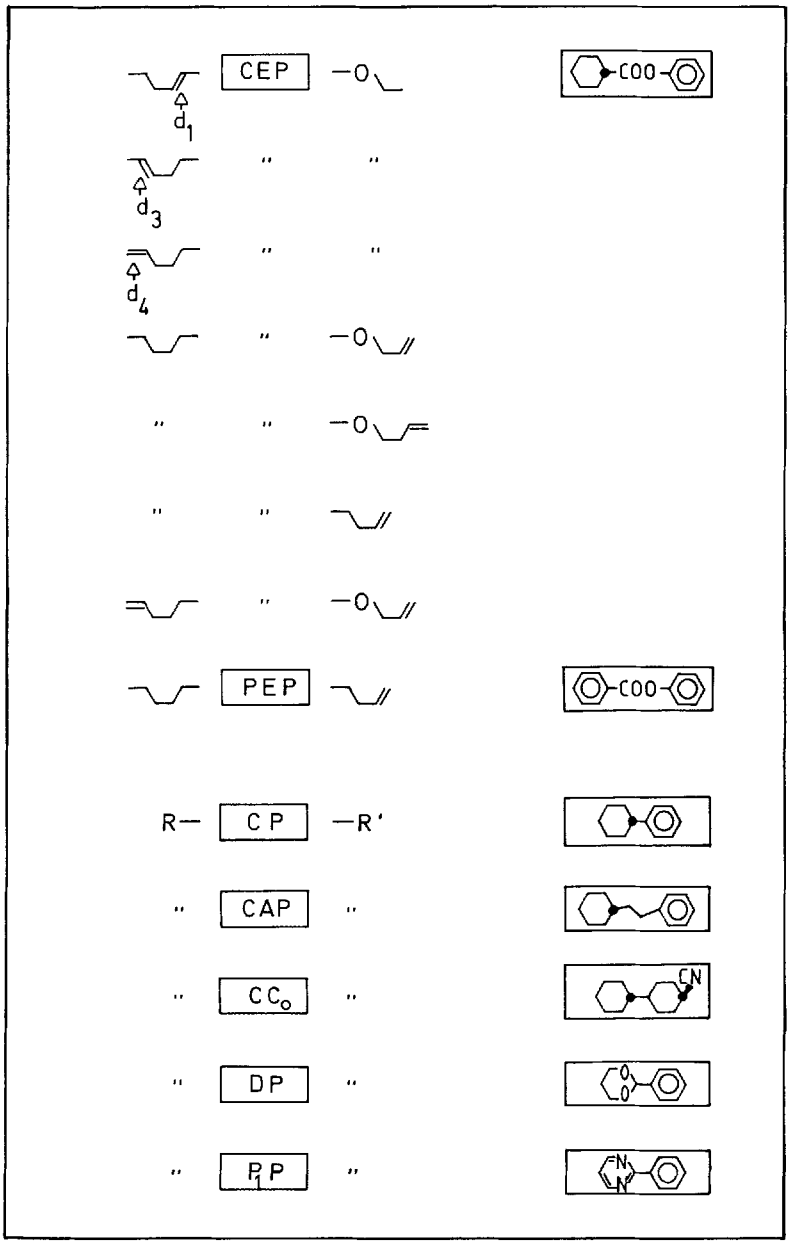
structures, macroscopic LC-material properties and display performance. Due to the complexity of liquid crystalline interactions, not adequately described by mean-field theories, correlations have to be found between specific molecular structural elements and the anisotropic optical, dielectric, viscous, elastic, etc., LC-material parameters. Based on such investigations, new liquid crystals and LC-mixtures can be designed.

We have shown earlier that different ring structures comprised in the 'rigid' core of LC-molecules strongly affect the elastic properties of nematics and, as one consequence, the multiplexability of twisted nematic displays (TN-LCDs) as well as their response times.[1,2] Recently we found that not only structural changes in the rigid core strongly affect the physical properties of liquid crystals, but perhaps even more so also structural changes in their flexible side-chains, namely the introduction of double bonds.[3,4] From the above investigations a number of new questions arose such as to what extent a reduction, or reversal of molecular polarity from strongly positive to only weakly, or strongly negative dielectric anisotropic would affect especially the elastic properties. Moreover, to what extent would the material properties be affected by the combination of different rigid cores with not only one, but with two flexible hydrocarbon side-chains comprising double bonds in either, or both of them (the positive dielectric alkenyls investigated first possess only one side-chain).[3,4,5] Another important question is the extent to which different ring systems in the rigid part of nonpolar molecules, especially heterocycles, would synergetically reduce the splay-bend elastic ratio k_3/k_1 when combined with alkenyl side-chains comprising double bonds in an appropriate position. We therefore designed a considerable number of new nematic liquid crystals with specific structural differences which cover a wide range of material properties. Due to their improved material parameters some of the new compounds will hopefully contribute to further enhanced performance of LCDs.

In the following the static dielectric constants $\epsilon_\parallel$ and $\epsilon_\perp$, the splay (k_1), twist (k_2) and bend (k_3) elastic constants, the optical anisotropy $\Delta n = (n_e - n_0)$ and in some representative cases also the bulk (η) and rotational viscosity (γ_1) of a number of new nonpolar alkenyls will be presented. Also included is a strongly negative dielectric anisotropic bicyclohexane alkenyl with an axially substituted CN-group. Table I schematically shows the molecular structural elements and the combinations of elements studied. The rectangles symbolize the different rigid cores that were combined with the respective alkenyl side-chains depicted in the left column of Table I. R and R' are alkyl

TABLE I

Schematic representation of molecular structural elements and combinations of elements investigated. The rectangles symbolize the different rigid cores.



or alkenyl chains respectively. The rectangles in the left column show the nomenclature used for the corresponding cores in the right column of Table I.

2. STRUCTURES OF NEW NEMATICS

Table II shows the alkenyl esters investigated. For comparison three reference esters[6] with saturated side-chains of different length are included. To exclude effects of different chain length[10] on the material properties, structures with identical chains should be compared. Where this is not possible, the effects of different lengths can be estimated from the three homologous XCEPY and the two homologous $\emptyset d_4$CEPO2 and $\emptyset d_4$CEPO3 (Table II). The esters in Table II include structures with a single double bond in either alkyl- or alkoxy side-chain, as well as the bis-alkenyl compound $\emptyset d_4$CEPO$d_3\emptyset$. Also included is the purely aromatic ester 5PEP$d_3\emptyset$.

Table III shows alkenyls comprising the heterocyclic pyrimidine and dioxane rings P_1 and *D* in their rigid cores. 5DPO4[7] at the bottom of Table III is used as reference with saturated side-chains. Because of the rather small mesomorphic range of the compounds in Table III, appropriate binary mixtures were made to investigate them.

Table IV shows directly and ethane linked phenylcyclohexane alkenyls as well as the laterally substituted bicyclohexane alkenyl 5CC$_o d_3\emptyset$. 5CPO2 and 5CAPO2[8] are used as saturated references. For a comparison of 5CC$_o d_3\emptyset$ in Table IV with its saturated counterpart, reference is made to Ref. 9.

3. DIELECTRIC, ELASTIC, VISCOUS AND OPTICAL PROPERTIES

3.1. Alkenyl esters

Figure 1 shows the temperature dependence of the static dielectric constants $\epsilon_\parallel$ and $\epsilon_\perp$ of some alkenyl esters and of the three binary mixtures m_4, m_8 and m_9 comprising heterocyclic alkenyls. As expected, most compounds exhibit a slightly negative dielectric anisotropy. The only exception is m_4 which is barely positively dielectric anisotropic due to nitrogen moments in the pyrimidine ring P_1 in $\emptyset d_4 P_1$P5.

Figure 2 shows the temperature dependences of the splay (k_1) and twist (k_2) elastic constants as well as that of the bend/splay elastic

TABLE II

Structures, melting (T_m) and clearing temperatures (T_c) of nematic alkenyl esters and three saturated reference compounds (bottom part).

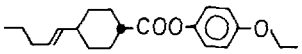
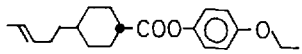
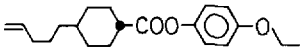
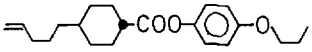
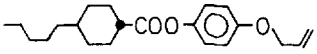
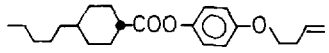
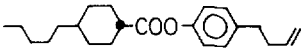
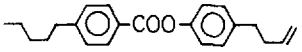
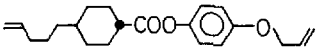
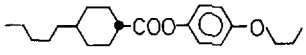
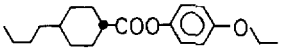
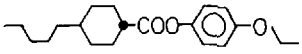
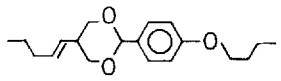
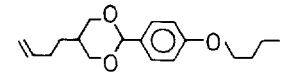
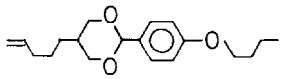
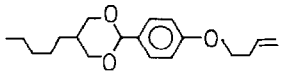
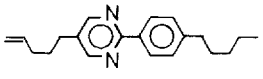
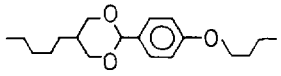
	Nomencl.	Structure	T_m	T_c
	$3d_1$CEPO2		57	92.0
	$1d_3$CEPO2		46	97.1
	$\not{o}d_4$CEPO2		33	58.3
	$\not{o}d_4$CEPO3		33	43.7
	5CEPO$d_3\not{o}$		34	80.0
	5CEPO$d_4\not{o}$		35	61.4
	5CEP$d_3\not{o}$		30	53.1
	5PEP$d_3\not{o}$		15	25.7
	$\not{o}d_4$CEPO$d_3\not{o}$		32	51.4
Reference LCs	5CEPO3		41	71.3
	4CEPO2		43	75.4
	5CEPO2		57	84.1

TABLE III

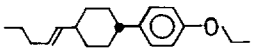
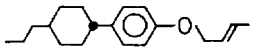
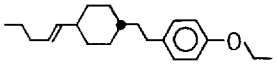
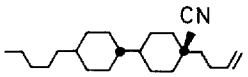
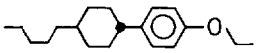
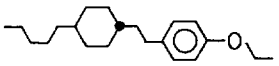
Nematic heterocyclic alkenyls comprising dioxane- and pyrimidine rings. 5DPO4 at the bottom is a saturated reference dioxane.

Nomencl.	Structure	T_m	T_c
$3d_1$DPO4		60	62·0
$\emptyset d_3$DPO4		36	36·7
$\emptyset d_4$DPO4		29	30·2
5DPO$d_4\emptyset$		31	35·2
$\emptyset d_4 P_1$P5		8	-4·5
5DPO4		42	52·9

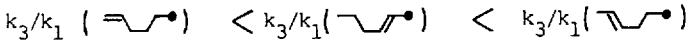
ratio (k_3/k_1) of alkenyl esters. Also included are data of the saturated reference ester 5CEPO3. The lack of any anomalous increase of k_1, k_2 or k_3/k_1 with decreasing temperature proves that there are no hidden smectic transitions adjacent to the nematic temperature range covered in Figure 2.[1] From Figure 2 follows that the elastic ratio k_3/k_1 strongly depends on the position of the double bond in the alkenyl chains. While a double bond in 4-position causes k_3/k_1 to markedly decrease compared with k_3/k_1 of the saturated reference compound (c.f. 5CEPO3 and $\emptyset d_4$CEPO3 for instance), a shift of the double bond into 3-position leads to a strong increase (c.f. 5CEPO3 and $1d_3$CEPO2). From Figure 2 also follows that an alkoxy oxygen can be replaced by a carbon atom without greatly affecting k_3/k_1 as long as the double bond position remains unchanged (c.f. 5CEPO$d_3\emptyset$ and 5CEP$d_3\emptyset$). This dependence of k_3/k_1 on the position of the double

TABLE IV

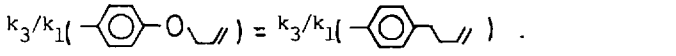
Nematic, directly- and ethane-linked PCH-alkenyls including the axially substituted $5CC_od_3\emptyset$ alkenyl.

Nomencl.	Structure	T_m	T_c
$3d_1CPO2$		32	56·5
$3CPOd_3^1$		42	57·5
$3d_1CAPO2$		25	43·9
$5CC_od_3\emptyset$		26	61·0
Reference LCs 5CPO2		51	49
5CAPO2		18	46·6

bond is—except for the much smaller values of k_3/k_1 in case of the above nonpolar esters—identical to that of polar nematics.[3,4] The reduction of the k_3/k_1-range in case of the alkenyl esters indicates that our earlier finding, according to which k_3/k_1 decreases within a given class of (saturated) liquid crystals upon reducing their polarity,[1] is also applicable to alkenyls. The dependence of k_3/k_1 on alkenyl position can be summarized by (c.f. also Table V):



and



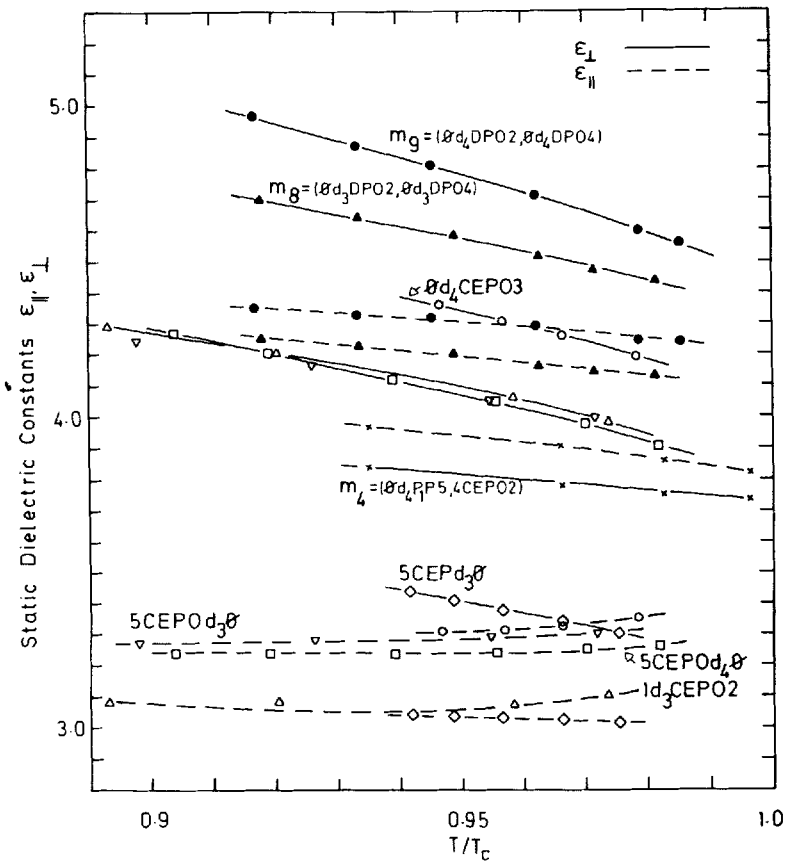


FIGURE 1 Temperature dependence of the static dielectric constants $\epsilon_\parallel$ and $\epsilon_\perp$ of alkenyl esters and three binary mixtures m_4, m_8 and m_9 comprising heterocyclic alkenyls. The respective values for $\epsilon_\parallel$ are dashed.

Table V summarizes the material properties of the alkenyl-esters depicted on Table II. Comparisons of the elastic, dielectric and optical properties are made at constant reduced temperature (T_c − 10°C), whereas—as far as determined—the bulk viscosity η and the rotational viscosity γ_1 are compared at T = 22°C = constant. The k_3/k_1-values of the 4-alkenyl esters which are low despite their rather short side-chains (Table V) make them—in combination with their small optical anisotropies, rather large mesomorphic ranges and rather low rotational viscosities—suitable for applications such as in highly multiplexed TN-LCDs operated in the first minimum. Comparing k_3/k_1 of 5CEPOd_3Ø and the bis-alkenyl Ød_4CEPOd_3Ø (Table V) shows

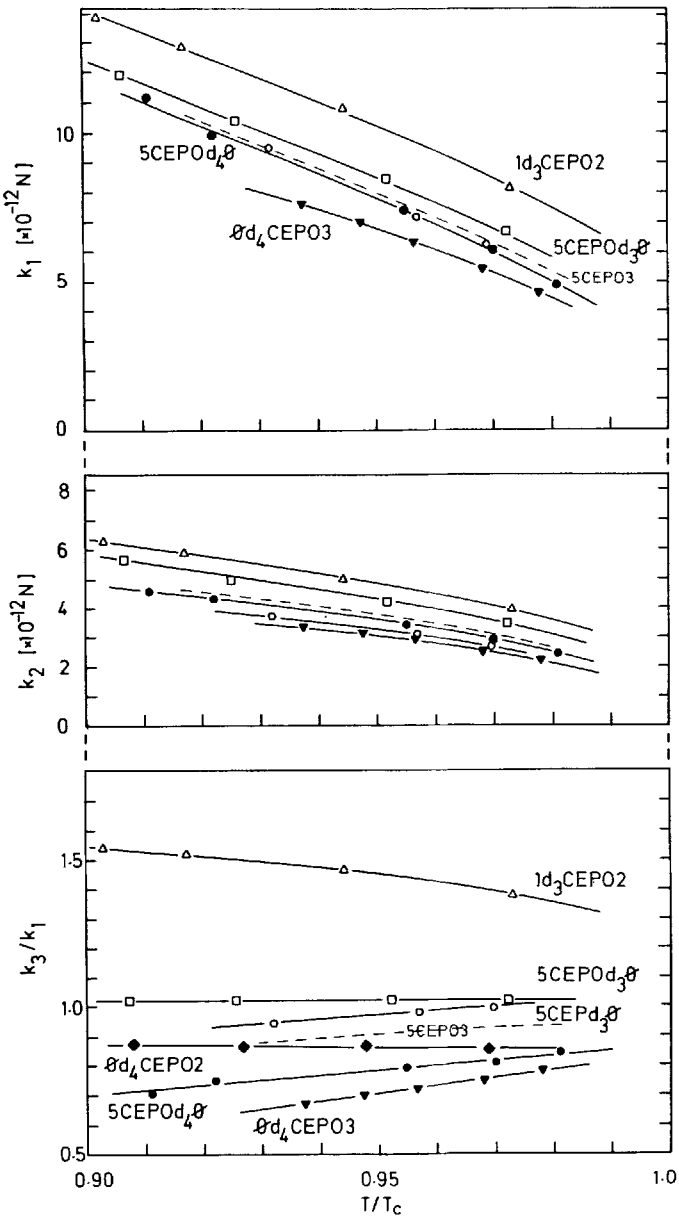


FIGURE 2 Temperature dependence of k_1, k_2 and k_3/k_1 of alkenyl esters. Data of saturated reference ester 5CEPO3 are included (dashed graphs).

TABLE V

Summary of material properties of alkenyl-esters. The elastic constants k_1, k_2, the elastic ratio k_3/k_1, the elastic expression $\varkappa = k_1 + (k_3 - 2k_2)/4$, the dielectric constants $\epsilon_\perp$, $\Delta\epsilon$ and the optical constants n_0, Δn were measured at $(T_c - 10°C)$ = constant, whereas the rotational (γ_1) and the bulk (η) viscosities were measured at $T = 22°C$ = constant.

LC	T_m	T_c	k_1	k_2	k_3/k_1	$\varkappa$	$\epsilon_\perp$	$\Delta\epsilon$	n_o	Δn	γ_1	η
$3d_1$CEPO2	57	92·0	6·05	2·75	1·23	6·5	4·01	-0·74	1·467	0·076		
$1d_3$CEPO2	46	97·1	8·18	3·92	1·38	9·0	3·98	-0·88	1·470	0·081		
$\mathscr{O}d_4$CEPO2	33	58·3	5·60	3·03	0·88	5·3	4·34	-0·96	1·482	0·065	120	
$\mathscr{O}d_4$CEPO3	33	43·7	5·43	2·51	0·75	5·2	4·24	-0·92	1·486	0·061	108	
5CEPO$d_4\mathscr{O}$	35	61·4	6·04	2·87	0·81	5·8	3·98	-0·73	1·475	0·062	125	31·5
5CEPO$d_3\mathscr{O}$	34	80·0	6·75	3·53	1·02	6·7	3·99	-0·70	1·471	0·068		23·5
5CEP$d_3\mathscr{O}$	30	53·1	6·22	2·60	0·99	6·5	3·32	-0·30	1·478	0·063		
5PEP$d_3\mathscr{O}$	15	25·7	6·49	3·62	1·17	6·6	4·69	+0·94	1·513	0·113		

ϕd_4CEPO$d_3\phi$	32	51·4			0·85				1·489	0·066		
5CEPO3	41	71·3	6·23	3·08	0·93	6·1	3·92	−0·82	1·468	0·062		
4CEPO2	43	75·4	5·93	3·14	1·05	5·9	4·20	−0·91	1·469	0·064	120	20·0
	$T = (T_C - 10°C)$										$T = 22°C$	

that the combination of double bonds in 3- and 4-position leads (i) to a reduction of k_3/k_1 (due to 4-position) and (ii) to an increase of the mesomorphic range (due to 3-position; c.f. also $\emptyset d_4$CEPO3). Thus, suitable combinations of double bonds can be used to achieve synergetic effects on material parameters. In Table V it is also interesting to note the large mesomorphic ranges and transition temperatures T_c of $3d_1$CEPO2 and $1d_3$CEPO2 compared with 4CEPO2.

3.2. Heterocyclic and axially substituted alkenyls; positive contrast guest-host mixtures

Figure 3 shows the temperature dependence of the elastic constants k_1 and k_2 and of the ratio k_3/k_1 of the binary mixtures m_4 and m_8–m_{10} containing the heterocyclic alkenyls depicted in Table III. For comparison the respective data of the binary 4-alkenyl mixture m_6 and those of m_5 are also included. m_5 comprises the laterally substituted alkenyl $5CC_od_3\emptyset$. From Figure 3 follows that the combination of heterocyclic rings—which themselves reduce k_3/k_1 compared with benzene, or hydrogenated rings[1]—with 4-alkenyls synergetically reduce k_3/k_1 drastically to values approaching 0.4! This holds for the 4-alkenyl-pyrimidine mixture m_4 in Figure 3, which has to be compared with the ester 4CEPO2 in Table V, as well as for the pure 4-alkenyl-dioxane mixtures m_9 and m_{10} with their exceptionally low k_3/k_1-values which are up to 50% lower than those of saturated dioxanes published in Ref. 1. Moreover, from m_8 and m_9 in Figure 3 follows that a shift of the double bond from position 4 into 3 increases k_3/k_1 in case of dioxanes analogously to the shift observed in the above alkenyl-esters. m_9 and m_{10} in Figure 3 also confirm the above finding that an alkoxy oxygen can be replaced by a carbon atom without greatly affecting k_3/k_1.

Regarding mixture m_5 in Figure 3, which comprises the axially substituted alkenyl $5CC_od_3\emptyset$, it is interesting to note not only the strong increase of k_1 and k_3 which this negative dielectric anisotropic alkenyl induces upon doping it with 4CEPO2 but also the remarkably strong increase of the twist elastic constant k_2 which in most LC-classes investigated so far does not vary much.[1,3,4,5] Because of the strong increase of both, k_1 and k_3, the ratio k_3/k_1 (m_5) remains surprisingly small for a 3-position alkenyl with two heterocyclic rings.

Table VI summarizes the material properties of binary mixtures m_1–m_{10}. Among the pure dioxane mixtures m_7–m_{10} it is only the 1-position alkenyl mixture m_7 that exhibits a slightly positive dielectric

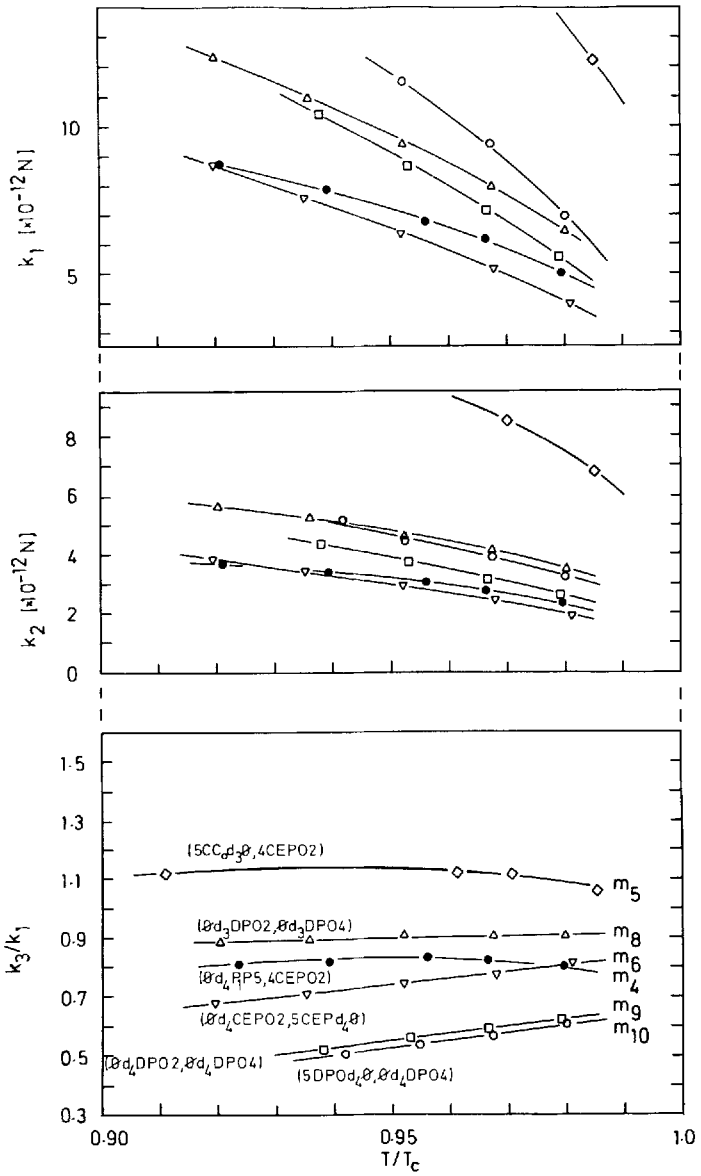


FIGURE 3 Temperature dependence of k_1, k_2 and k_3/k_1 of heterocyclic binary mixtures m_4 and m_8–m_{10}. Mixture m_5 contains the axially substituted alkenyl 5CC$_o d_3$Ø.

TABLE VI

Summary of material properties of binary mixtures m_1–m_{10}. The molar proportions chosen for m_1–m_6 and m_{10} are (50%, 50%), whereas those of m_7–m_9 are (40%, 60%). Except for the viscosities γ_1 and η (η in brackets) which were measured at T = 22°C the material constants were determined at (T_c − 10°C) = constant.

Mixture	T_m	T_c	k_1	k_2	k_3/k_1	$\varkappa$	$\varepsilon_\perp$	$\Delta\varepsilon$	n_o	Δn	γ_1 (η)
m_1 = (5DPOd$_3$Ø, 4CEPO2)	<0	55·3	6·43	2·97	0·94	6·5	4·36	−0·29	1·480	0·071	125
m_2 = (5DPOd$_4$Ø, 4CEPO2)	<0	48·7	6·17	2·98	0·89	6·1	4·28	−0·32	1·481	0·068	119
m_3 = (Ød$_4$ DPO3, 4CEPO2)	<0	38·1	8·14	4·08	0·83	7·8	4·42	−0·74	1·487	0·067	95
m_4 = (Ød$_4$P$_1$P5, 4CEPO2)	12	23·0	6·09	2·70	0·82	6·0	3·78	0·12	1·505	0·097	– (25)
m_5 = (5CC$_o$d$_3$Ø, 4CEPO2)	<5	65·0	15·8	8·49	1·11	16·0	6·97	−2·80	1·470	0·045	139 (35)
m_6 = (Ød$_4$CEPO2, 5CEPd$_4$Ø)	<0	36·9	5·09	2·39	0·78	4·9	3·88	−0·66	1·488	0·058	
m_7 = (3d$_1$DPO2, 3d$_1$DPO4)	−30	61·6	8·06	3·65	0·89	8·0	3·92	0·36	1·476	0·088	

m_8= (8d$_3$DPO2, 8d$_3$DPO4)	< 5	32·8	7·88	4·08	0·90	7·6	4·49	-0·34	1·492	0·084	
m_9= (8d$_4$DPO2, 8d$_4$DPO4)	< 0	26·3	7·12	3·13	0·56	4·6	4·68	-0·40	1·495	0·074	
m_{10}= (5DPOd$_4$8, 8d$_4$DPO4)	-11	32·0	9·38	3·89	0·56	8·8	4·38	-0·05	1·489	0·074	
	T = (T$_c$ - 10°C)										T = 22°C

anisotropy $\Delta\epsilon = 0.36$. m_7 is also the only heterocyclic mixture with an ordinary index of refraction as low as $n_0 = 1.476$ in Table VI. Since the rigid cores in m_7–m_{10} are identical, the change of sign of $\Delta\epsilon$ (m_7) can only be attributed to a reduced angle between the nematic director $\hat{n}$ and the 1-position (conjugated) double bond d_1 compared with the respective angles of d_3 and d_4. As a consequence the induced dipole moment contributing to $\epsilon_\parallel$ in d_1-dioxanes increases and n_0 decreases. This finding qualitatively corresponds with experimental data and molecular graphics modelling performed with polar alkenyls[3] which also indicated that the equilibrium angles between C=C double bonds and $\hat{n}$ are positional dependent.

A comparison of the elastic expressions $\varkappa = k_1 + (k_3 - 2k_2)/4$ of the alkenyls in Table V and VI shows, that $\varkappa(m_5) = 16$ is by far the largest among all of them. $\varkappa(m_5)$ is not only three times larger than $\varkappa$(4CEPO2)—m_5 consists of 50% 4CEPO2—it is even larger than the exceptionally large $\varkappa$-values which we found for cyano-ethanes of the type Xd_3CAP.[3] Therefore, and because of the rather small rotational viscosity $\gamma_1(m_5)$, which is comparable to γ_1(4CEPO2), small visco-elastic ratios $\gamma_1/\varkappa$ result for m_7. Thus, short electro-optical response times and large electro-optical thresholds can be expected when using 5CC$_o d_3\emptyset$ in mixtures for TN-LCDs.[3] Moreover, because of the small values of γ_1, and Δn of 5CC$_o d_3\emptyset$ and because of the strong negative dielectric anisotropy $\Delta\epsilon$(5CC$_o d_3\emptyset$) $\simeq -4.4$ at ($T_c - 10$°C), such broad range (Table IV) axially substituted alkenyls are of interest for positive contrast guest-host mixtures.

Figure 4 shows the respective spectra for light polarized parallel ($P_\parallel$) and perpendicular ($P_\perp$) to the nematic director of the new, negative dielectric anisotropic guest-host mixture 1319 comprising axially substituted nematics of the type XCC$_o d_3\emptyset$. Compared with other positive contrast mixtures, Figure 4 shows that 1319 exhibits unusually large order parameters $0.72 \leq S \leq 0.78$ over the entire visible spectral range. 1319 comprises the same dichroic dyes as our negative contrast black ethane-mixture 1270[11] the high order parameters $0.76 \leq S \leq 0.79$ of which are not much larger than those of 1319. The comparably large S-values induced by the two entirely different hosts therefore show that the axially substituted alkenyls in the host of 1319 hardly disturb the favourable dye orientation and the high constrast of the guest-host mixture. From the data in the caption of Figure 4 follows that 1319 exhibits a low viscosity and a broad mesomorphic range. Both of these properties render 1319 applicable for outdoor applications.

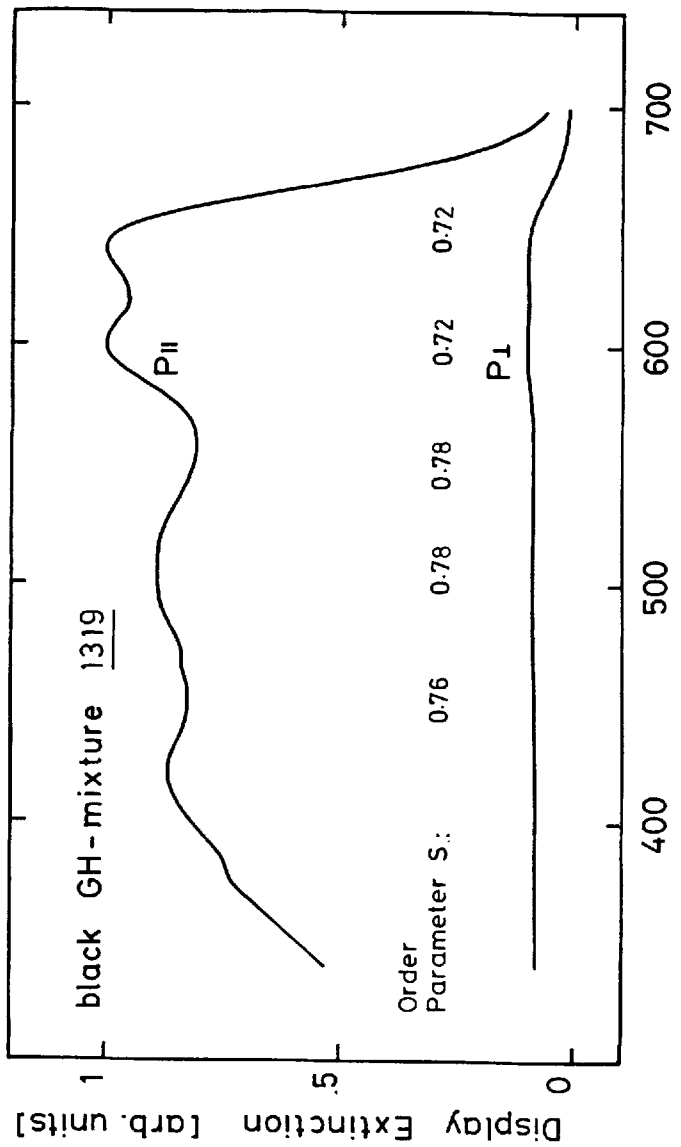


FIGURE 4 Absorption spectra of positive contrast, black guest-host mixture 1319 for light polarized parallel ($P_{\parallel}$) and perpendicular ($P_{\perp}$) to the nematic director. 1319 exhibits the following data at 22°C: $\epsilon_{\parallel} = 3.41$, $\Delta\epsilon = -3.05$, $n_0 = 1.488$, $\Delta n = 0.081$, $k_3/k_1 = 1.16$, $\eta = 40$ cP, $V_t = 2.45$ volts. The melting and clearing temperatures are ($T_{\%}$, T_c) = (−30°C, 92°C).

3.3. PCH- and ethane-linked alkenyls; rotational viscosities

Table VII shows the material properties of two PCH-alkenyls and of the ethane-linked alkenyl $3d_1$CAPO2. A comparison between the mesophases of $3d_1$CPO2 and 3CPO$d_3$1 in Table VII with the monotropic saturated compound 5CPO2 (Table IV) shows that the introduction of d_1 and d_3 remarkably improve the nematic ranges. In case of $3d_1$CAPO2, melting and clearing temperatures are comparable to those of its saturated counterpart 5CAPO2. The bulk viscosities η depicted in Table VII are up to three times smaller than η of the low-viscous esters in Table V. Since the rotational viscosity γ_1(5CAPO2) is also considerably lower than γ_1 of the esters in Table V, the alkenyls in Table VII can be expected to be very fast indeed when used in LCDs. From the above and from Ref. 3, $\varkappa$ of ethane-linked alkenyls of the type Xd_3CAPOY can be expected to be still larger than $\varkappa(3d_1\text{CAPO2})$. Thus, still further improved visco-elastic ratios $\gamma_1/\varkappa$ and therefore still shorter response times can be expected.

Figure 5 shows the temperature dependence of the rotational viscosities γ_1 of the binary mixtures m_1, m_3 and m_5, of the single ester components 4CEPO2, $\emptyset d_4$CEPO2, $\emptyset d_4$CEPO3 and of the saturated ethane 5CAPO2. From Figure 5 follow comparable activation energies for the mixtures and ester components at $T \ll T_c$; whereas the activation energy of 5CAPO2 is slightly smaller. In analogy to polar alkenyls[3] Figure 5 shows that the two 4-alkenyl esters $\emptyset d_4$CEPO2 and $\emptyset d_4$CEPO3 exhibit lower γ_1-values than the saturated ester 4CEPO2. What is surprising, is that $\gamma_1(\emptyset d_4\text{CEPO3}) < \gamma_1(\emptyset d_4\text{CEPO2})$, this despite the larger alkoxy chain of the former. From $\gamma_1(\text{4CEPO2}) > \gamma_1(m_1) > \gamma_1(m_3)$ follows (i) that the rotational viscosities of both alkenyldioxanes $\emptyset d_4$DPO3 and 5DPO$d_3\emptyset$ are lower than γ_1 of the saturated ester 4CEPO2 and (ii) $\gamma_1(\text{5DPO}d_3\emptyset) > \gamma_1(\emptyset d_4\text{DPO3})$, which confirms our earlier findings with polar d_3 and d_4-alkenyls.[3] In Figure 5 it is interesting to note the virtually identical γ_1-values of m_5 and 4CEPO2. This shows that the rotational viscosity of the axially substituted nematic 5CC$_o d_3\emptyset$ is comparable to that of 4CEPO2, this despite its much larger negative dielectric anisotropy (Table VI) which often leads to large viscosities. For reference purposes one should note that γ_1(4CEPO2) is virtually identical with the rotational viscosity of the cyano-PCH 5CP.[3]

4. STABILITY OF ALKENYLS

Double bonds which are in conjugation with each other or in conjugation with π-electrons of aromatic rings are well known to be

TABLE VII

Summary of material properties of PCH- and ethane-linked alkenyls. The saturated compound 5CAPO2 is used as reference. Except for η and γ_1 (γ_1 in brackets) which were determined at 22°C, the material parameters were measured at (T_c − 10°C) = constant.

LC	T_m	T_c	k_1	k_2	k_3/k_1	$\varkappa$	$\varepsilon_\perp$	$\Delta\varepsilon$	n_o	Δn	η (γ_1)
$3d_1CPO2$	32	56·5	6·32	3·53	1·30	6·6	3·18	-0·17	1·485	0·085	11·8
$3CPOd_31$	42	57·5	10·86	5·60	1·14	11·2	3·06	-0·33	1·486	0·090	
$3d_1CAPO2$	25	43·9	8·86	4·00	1·43	10·0	3·05	-0·22	1·485	0·087	11·8
5CAPO2	18	46·6	10·15	5·20	1·07	10·3	2·98	-0·24	1·480	0·072	12·0 (79)
	T = (T_c -10°C)										T = 22°C

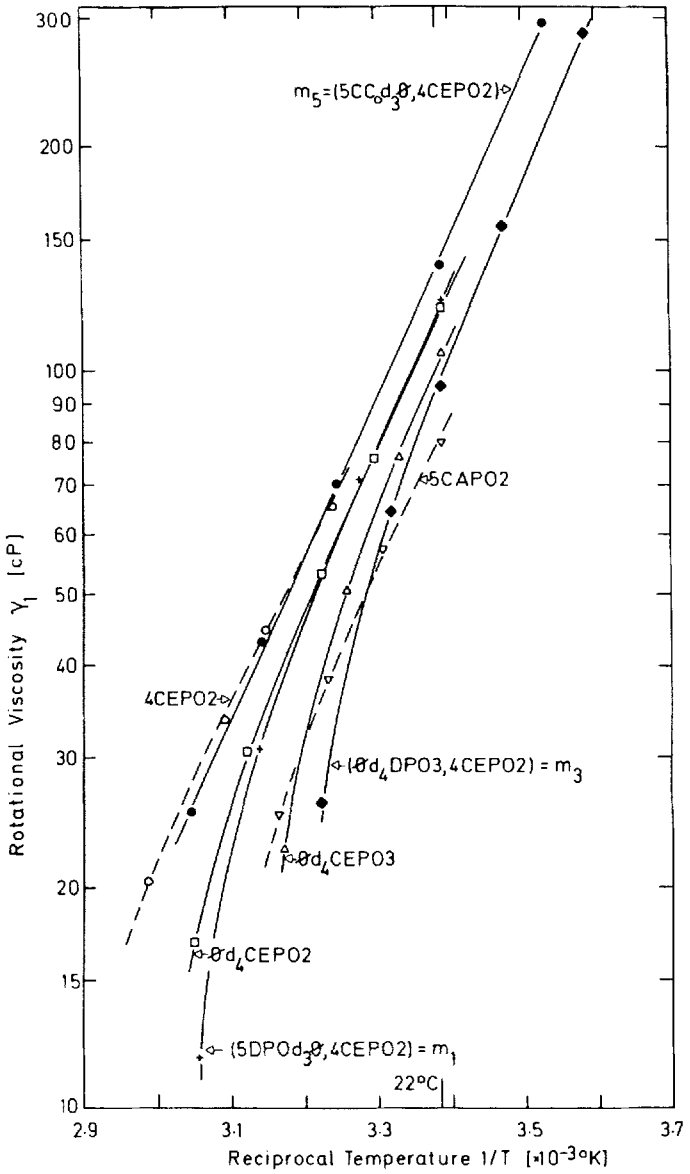
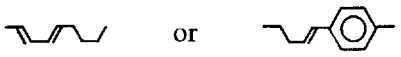


FIGURE 5 Temperature dependence of rotational viscosity γ_1 of binary mixtures m_1, m_3, m_5, of the components 4CEPO2, Ød_4CEPO2, Ød_4CEPO3 and 5CAPO2. The saturated reference graphs are dashed.

susceptible to photochemical reactions which create trans-cis isomers. However, isolated double bonds, which absorb light only at very low wavelength $\lambda \simeq 205$ nm, i.e. at considerably lower wavelengths than a benzene ring for instance ($\lambda = 254$ nm), are photochemically stable under display conditions where light with $\lambda \lesssim 320$ nm is blocked not only by the glass but even more so by polarizers or electrode layers. A prerequisite for the design of photochemically stable alkenyl liquid crystals is therefore to avoid conjugated double bonds, such as structures like



In both of these (trans) cases, strong UV-illumination creates cis-isomers which in case of liquid crystals would lead to a depression of the nematic-isotropic transition temperature T_c.

To verify the stability of isolated double bonds in liquid crystals we performed illumination tests and heating tests with alkenyl mixtures as well as with well known reference compounds. For the illumination tests we used a Hanau Suntest apparatus providing a light intensity of 830 W/m^2 from a 1.1 kW Xenon arc at an illumination distance of 23 cm from a room temperature reflective base plate. The mixtures were tested in vacuum filled, 8 μm spaced LCDs which were protected neither by polarizing sheets nor by other cut-off filters. The heating tests were performed at 120°C. The LC-parameters monitored were the clearing temperature T_c and the LCD current. The following mixtures were used for the experiments: $\alpha = (M, 2d_1\text{CP})$, $\beta = (M, 1d_3\text{CP})$, $\delta = (5\text{CC}_o d_3 \emptyset, \text{4CEPO2})$, $\vartheta = (M, \text{5PP})$ in molar proportions $(M, X) = (60\%, 40\%)$. Host mixture M = (3CP, 5CP, 7CP, 5CPAC4) contains only chemically and photochemically most stable and widely used phenylcyclohexanes[12] and ethanes.[11] Mixture ϑ containing the cyanobiphenyl 5PP served—like mixture M—as a reference. Except for δ the tests were performed with positive dielectric CN-nematics because they are in general more susceptible to rough environmental conditions than their nonpolar counterparts. The nomenclature used for the cyano compounds is the same as in reference 3; for example 5CP = pentyl-cyano-phenylcyclohexane and 5PP = pentyl-cyano-biphenyl. Three commercial watch TN-LCDs were used for each heating and illumination test. Due to rather strong variations of the quality of the alignment layers of the LCDs, the conductivities among different LCDs varied quite considerably. The results from each set of three LCDs were averaged.

The two upper parts of Figure 6 show the depression ΔT_c of the clearing temperature T_c of each of the five mixtures M, α, β, δ and

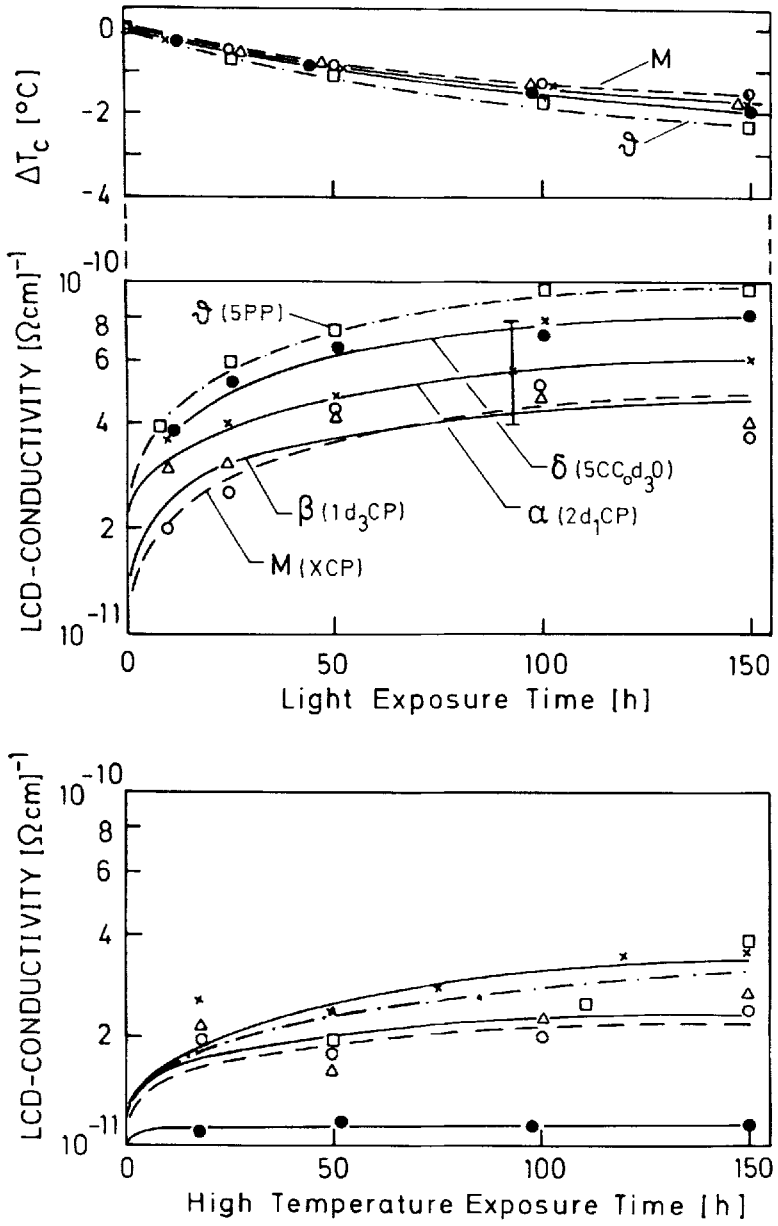


FIGURE 6 Depression ΔT_c of clearing temperature T_c of alkenyl mixtures α, β, δ and of saturated reference mixtures *M* and ϑ (dashed graphs) under light illumination (top). Specific LCD-conductivity at 22°C under light illumination (middle). Specific LCD-conductivity at 22°C after storage at 120°C (bottom).

ϑ, as well as the increase of LCD-conductivity with time upon light exposure of the displays. The graphs $\Delta T_c(t)$ show that the CN-biphenyl reference mixture ϑ is more susceptible to light illumination than either of the two polar alkenyl mixtures α and β or the negative dielectric alkenyl mixture δ. Actually, the ΔT_c-depressions of the alkenyl mixtures are comparably low as those of the PCH-ethane reference mixture *M*. This shows that isolated alkenyl double bonds remain isolated in the liquid crystalline environment. They do not form conjugated systems, for instance with adjacent benzene rings from other molecules, which could lead to trans-cis isomers and thus to a depression of T_c. From the middle part of Figure 6 follows that also the increase of LCD-conductivity of alkenyl mixtures—which is probably more due to residual impurities in the LC-materials and/or to ionic impurities penetrating from the LCD surfaces into the LC-materials than due to photochemical reactions of the LC-molecules themselves—is comparable to the current increase of reference mixtures *M* and ϑ. However, it should be noted in Figure 6 that despite the increase of current the currents saturate at still very low conductivity levels $\sigma \lesssim 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

Because the depression of clearing temperatures during the heating tests remained below 1°C for all mixtures after 150 hours of exposure to 120°C, the data are not plotted in Figure 6.

The bottom part of Figure 6 shows the increase of LCD-current measured at 22°C after high temperature exposure of the LCDs. As with the illumination tests no significant changes occurred compared with the reference mixtures. In Figure 6 it is interesting to note the remarkably small and constant conductivity of mixture δ comprising $5CC_od_3\emptyset$. This confirms the above mentioned observation that non-polar or—as in this case—even negative dielectric anisotropic mixtures often exhibit smaller current increases under heating test conditions than strongly positive dielectric materials. This trend is likely due to the smaller ion-solubility of materials with small $\Delta\epsilon$; i.e. since the inner display surfaces act as ion-sources, they have to be perfectly clean to avoid any penetration of ions into the LC-dielectric. Like with cyano biphenyls which photochemically decompose when simultaneously exposed to oxygen and light;[13] oxygen was excluded from the alkenyl mixtures by using sealed LCDs for the above tests.

5. CONCLUSIONS

From the design of specific molecular structures and from investigations into the dielectric, birefringence, viscous and all three elastic

constants we have shown that a wide range of material properties result in nonpolar alkenyl nematics, including unusually low values of k_3/k_1 and large twist elastic constants k_2. The reduction of molecular polarity and its reversal from positive dielectric anisotropic to negative, the introduction of double bonds in either, or both of two hydrocarbon side-chains—including alkoxy oxygens—as well as the combination of different rigid molecular cores with appropriate double bond positions in the chains were shown to synergetically affect especially the elastic properties of the new compounds. From combining heterocyclic ring systems with chains comprising double bonds in 4-position, elastic ratios as low as $k_3/k_1 \simeq 0.4$ result. Moreover, since only short side-chains had to be used to achieve low elastic ratios, the rotational viscosities γ_1 of the resulting nematics remained low too. Therefore, and due the large elastic expressions $\varkappa = k_1 + (k_3 - 2k_2)/4$ of some of the compounds, very short electro-optical response times in TN-LCDs are expected. The low optical anisotropies Δn combined with the low k_3/k_1-ratios of heterocyclic 4-alkenyls render them applicable for highly multiplexing TN-LCDs in the first minimum, i.e. in an operating mode providing a wide range of view.

Moreover, we have shown that the broad range, negative dielectric anisotropic, laterally substituted alkenyls $XCC_od_3\emptyset$ do hardly disturb the favourable orientation of dichroic dyes when used in positive contrast guest-host mixtures. Thus, large order parameters $0.72 \leq S \leq 0.79$ over the entire visible spectrum of black, positive contrast guest-host mixtures were achieved. We have also shown that the stability of alkenyls comprising non-conjugated bonds is comparable to that of the corresponding saturated compounds. No trans-cis isomerization that would lead to a depression of clearing temperature was found.

Acknowledgments

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