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M. Schadt [a], M. Petrzilka [a], P. R. Gerber [a] & A. Villiger [a]
[a] Central Research Units, F. Hoffmann-La Roche & Co. Ltd., CH-4002, Basel, Switzerland
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Polar Alkenyls: Physical Properties and Correlations with Molecular Structure of New Nematic Liquid Crystals†

M. SCHADT, M. PETRZILKA, P. R. GERBER and A. VILLIGER

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

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The elastic constants k_{11}, k_{22}, k_{33}, the bulk and rotational viscosities, the birefringence, the static dielectric and electro-optical properties in TN-LCDs of new, positive dielectric and electro-optical properties in TN-LCDs of new, positive dielectric nematic liquid crystals, namely polar alkenyls, are reported. The molecules comprise a double bond in their hydrocarbon side chain as well as different rigid cores, namely directly- and ethane linked PCH-cores as well as heterocyclic (dioxane) cores. Despite their dielectric and conformational similarity, large variations of the elastic constants depending on the position of the alkenyl double bond are shown to result in alkenyls with PCH cores. This leads to variations of k_{33}/k_{11} and $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ among different alkenyls with the same chain length of almost a factor of 2 at constant reduced temperature (T_c-10°C). From molecular modelling follow rod-shaped van der Waals conformations with constant length/width ratio L/W for all directly linked alkenyls. Therefore, and due to $k_{33}/k_{11} \neq$ constant, nematic hard-rod models neglecting molecule-specific interactions and implying $k_{33}/k_{11} \propto L/W$ are qualitatively shown to be inadequate to explain the elastic ratios of nematics. Despite up to 30% larger optical anisotropies the response times of some alkenyls in TN-LCDs are ~30% shorter than those of PCHs. This result is not primarily due to the low rotational viscosity γ_1 of alkenyls but rather due to their low visco-elastic ratios γ_1/κ. The fast response and the wide range of elastic properties render the stable polar alkenyls applicable for highly multiplexed as well as fast responding LCDs.

1. INTRODUCTION

Polar nematic liquid crystals comprising molecules with structural elements leading to strong longitudinal permanent dipole moments

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exhibit the positive dielectric anisotropy $\Delta\epsilon = (\epsilon_{\parallel} - \epsilon_{\perp})$ that is required for most LCD applications. From correlations of material properties with molecular structures of polar and nonpolar representatives of the same liquid crystal class we found that polar groups not only determine $\Delta\epsilon$ but also strongly affect the elastic constants and the viscosity of nematics. Thus, in structurally comparable liquid crystals the bend/splay elastic ratio k_{33}/k_{11} decreases within a given class when reducing the polarity and thus $\Delta\epsilon$ of the molecules.[1] Moreover, k_{33}/k_{11} is affected by the type of ring structures of which the rigid part of the molecules consists.[1] As a consequence, and especially in cases where heterocyclic rings are involved, low elastic ratios k_{33}/k_{11} and therefore steep electro-optical characteristics in twisted nematic displays (TN-LCDs) can be achieved. Apart from $\Delta\epsilon$ and specific structural elements, k_{33}/k_{11} of nematics is also affected by the number of carbon atoms in alkyl side chains. De Jeu et al. who investigated a homologous series of nonpolar azoxybenzenes found k_{33}/k_{11} to decrease with increasing chain length.[2] An analogous behaviour was reported[3] for polar phenylcyclohexanes[4] (PCHs). As the dielectric and elastic properties, the bulk viscosity η[5,6] as well as the rotational viscosity γ_1[7] are also affected by polar groups. Thus, nematics with $\Delta\epsilon \gg 0$ exhibit in general considerably larger viscosities than their nonpolar counterparts.

Regrettably, there seem to be no theoretical model calculations in the literature extending mean-field theories as those of Maier and Saupe,[8] Priest[9] or Straley[10] which would take into account specific molecular interactions, i.e. induced dipole-dipole or permanent dipole interactions. From the calculations of Priest[9] and Straley[10] who included higher order terms in the intermolecular mean-field potential of the Onsager hard rod model which holds for extremely long rods, one is temped to conclude[11] that k_{33}/k_{11} increases in nematics with increasing length to width ratio L/W of the (short) nematic rods and/or with increasing L/W ratio of hypothetical sterical units.[19] However, the above cited experiments[1,2,3] performed with dielectrically and structurally distinct but comparable classes indicate that geometrical considerations alone are inadequate to predict the important elastic ratios of nematic liquid crystals. Molecular-specific interactions have to be taken into account.

In the following the properties of five new polar nematic liquid crystal families with rather unusual elastic and viscous behaviour synthesized in our laboratories are presented, namely cyano alkenyls. The classes differ from each other with respect to the position of the alkenyl double bond in the hydrocarbon side chain and/or with

respect to their rigid core which consists either of a PCH ring system, an ethane linked ring system or a phenyl-dioxane ring system. The elastic ratio k_{33}/k_{11} as well as the elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ of polar alkenyls are shown to depend strongly on the position of the double bond; i.e. on a seemingly minor structural modification. Moreover, their low rotational viscosities are also shown to depend on alkenyl position. From the low viscoelastic ratios γ_1/κ of some alkenyls, response times of TN-LCDs result which are up to 30% lower than those of the fast responding PCHs. We show that the large range over which k_{ii} of the dielectrically and sterically similar new compounds varies is incompatible with the constant L/W ratio of their rod shaped van der Waals radii determined with an interactive molecular graphics modelling system.

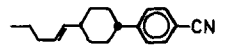
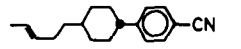
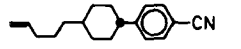
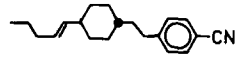
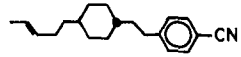
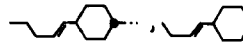
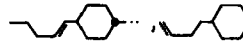
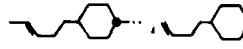
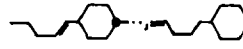
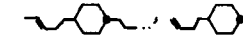
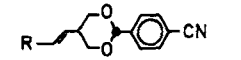
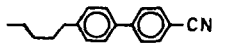
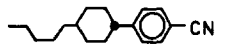
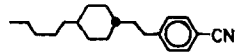
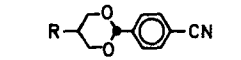
2. EXPERIMENTAL

2.1. Structures of nematics

The upper part of Table I depicts the cyano alkenyls chosen for our investigations. For comparison the lower part shows cyano compounds exhibiting the same rigid core as the alkenyls, namely PCHs,[4] ethanes[12] and dioxanes;[14] also included is a biphenyl.[13] To avoid effects caused by different hydrocarbon chain lengths, the chains of all individual components are identical, they comprise five carbon atoms. Table I shows three different PCH type alkenyls namely $3d_1$CP, $1d_3$CP and $Ød_4$CP. The only difference among them lies in the position of the alkenyl bond d_x where x denominates the position of the double bond from the respective cyclohexane ring C (c.f. nomenclature in caption of Table I). For the investigation of monotropic or barely nematic compounds, binary mixtures were made of components whose number of chain carbon atoms differ by 1. To allow comparisons with earlier reported investigations[1] on other LC-classes molar proportions of (60/40) were used (Tab. I). The positional influence of the alkenyl double bond was investigated with mixtures m_1–m_4 exhibiting comparable nematic temperature ranges $T_m \ldots T_c$ (Tab. I). m_1 comprises alkenyls in 1-position only, whereas m_2 is a combination between position 1 and 3; m_3 is a pure 3-alkenyl mixture and m_4 combines position 1 with 4. The directly linked and the ethane linked 3-position alkenyl mixtures m_3 and m_5 are used to study the influence of the (flexible) ethane linkage on alkenyls.

TABLE I

Single components (100%) and binary mixtures (60% mol/40%) with their respective melting and nematic-isotropic transition temperatures T_m and T_c. The following nomenclature is used for the structural elements: C = cyclohexane ring, P = phenyl ring, B = biphenyl, D = dioxane ring, A = ethane linkage and d_x = alkenyl double bond with x defining its position in the chain (increasing x corresponds to a shift of the double bond away from the rigid core). The numbers in front of d_x are those of the carbon atoms attached to the double bond. In case of alkyl side chains they denominate the total number of carbon atoms in the chain.

COMPOSITION	MOL.PROP.	STRUCTURE	T_m[°C]	T_c[°C]	REF.
$3d_1CP$	100%		16	58.5	
$1d_3CP$	100%		60	73.7	
$\varnothing d_4CP$	100%		30	10.2	
$3d_1CAP$	100%		25	47.5	
$1d_3CAP$	100%		44	65.5	
$m_1=(3d_1CP,2d_1CP)$	(60,40)		<5	52.2	
$m_2=(3d_1CP,\varnothing d_3CP)$	(60,40)		<5	50.9	
$m_3=(1d_3CP,\varnothing d_3CP)$	(60,40)		38	65.2	
$m_4=(3d_1CP,\varnothing d_4CP)$	(60,40)		-5	35.1	
$m_5=(1d_3CAP,\varnothing d_3CAP)$	(60,40)		-25	57.7	
$m_6=(4d_1DP,3d_1DP)$	(60,40)		-35	45.3	
K15 (=5B)	100%		24	34.8	[13]
PCH5 (=5CP)	100%		30	54.8	[4]
5CAP	100%		31	52.5	[12]
$m_7=(4DP,5DP)$	(60,40)		-27	40.5	[14]

novel liquid crystals

2.2. Dielectric, elastic and viscous properties of binary alkenyl mixtures

Figure 1 shows the temperature dependence of the static dielectric constants $\epsilon_\perp$ and $\Delta\epsilon$ of alkenyl mixtures m_1–m_5. For comparison, measurements of the cyano biphenyl K15 are included. The results show—except for a more pronounced temperature dependence $\Delta\epsilon\,(T)$ of m_4 which approaches that of K15—no significant variations of either $\epsilon_\perp$ or $\Delta\epsilon$ among m_1–m_5.

In Figure 2 the temperature dependences of the splay (k_{11}) twist (k_{22}) and bend (k_{33}) elastic constants of mixtures m_1–m_5 are depicted. The lack of smectic pretransitional increases[1] of k_{ii} in Figure 2 with decreasing temperature proves that mixtures m_1–m_5 are indeed nematic in the temperature range studied. From Figure 2 follows that all three elastic constants strongly depend on the position of the alkenyl double bond. When shifting the double bond from position $1 \rightarrow 3 \rightarrow 4$ the following order results:

$$k_{ii}(m_4) < k_{ii}(m_1) < k_{ii}(m_2) < k_{ii}(m_3) < k_{ii}(m_5).$$

Thus, a shift of the double bond from position $1 \rightarrow 3$ causes k_{11}, k_{22} and k_{33} to strongly increase. The increase is least pronounced for k_{22} and strongest for k_{33} (c.f. m_1–m_3 in Fig. 2). The incorporation of an ethane linkage in the rigid core of 3-alkenyls, further pronounces this

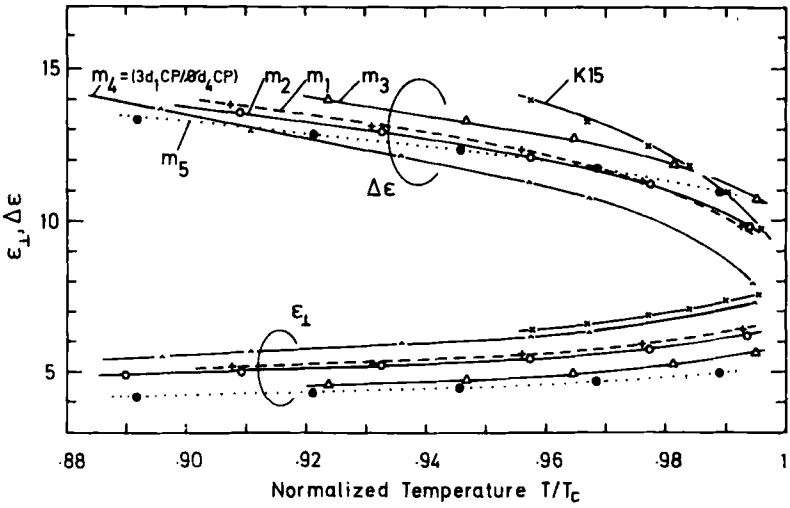


FIGURE 1 Temperature dependence of the static dielectric constants $\epsilon_\perp$, $\Delta\epsilon = (\epsilon_\parallel - \epsilon_\perp)$ of alkenyl mixtures m_1–m_5 and of the biphenyl K15.

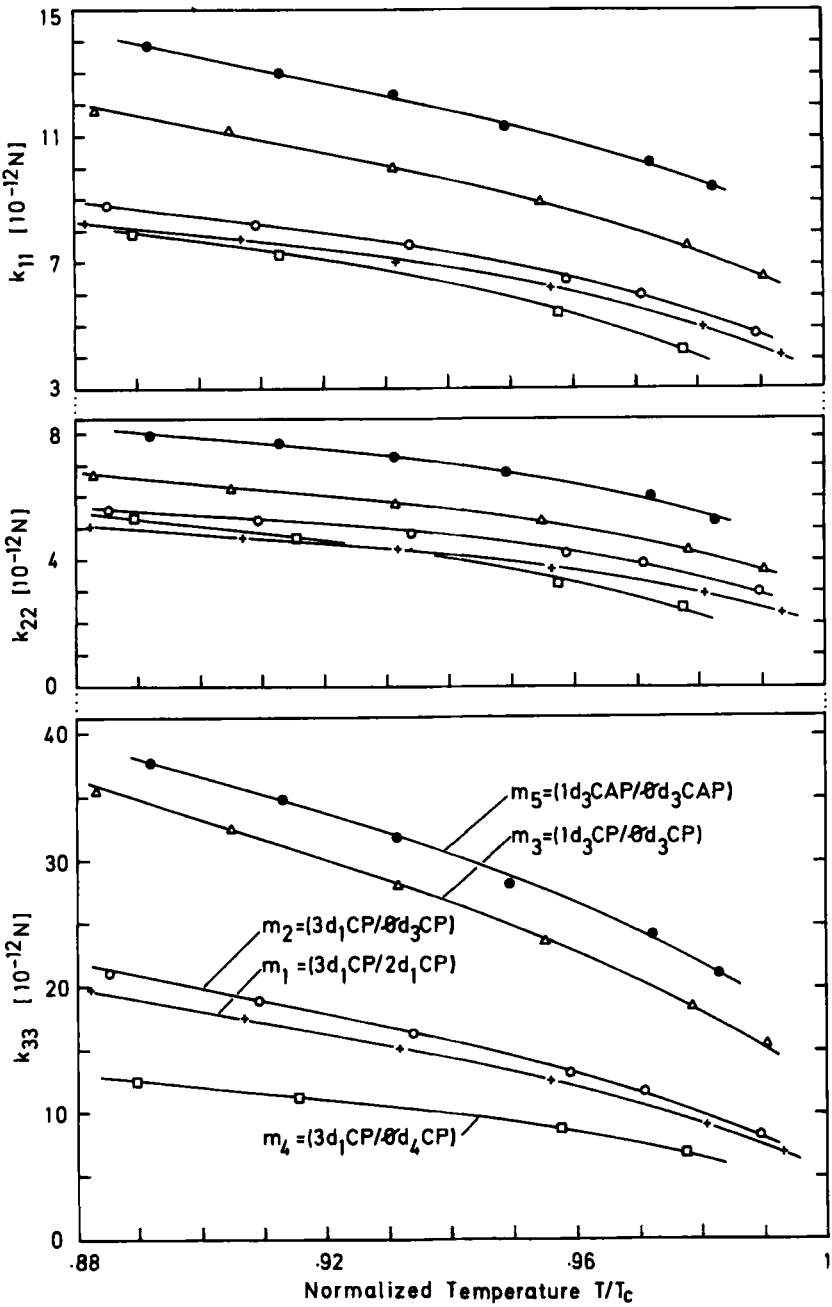


FIGURE 2 Temperature dependence of the splay (k_{11}), twist (k_{22}) and bend (k_{33}) elastic constants of alkenyl mixtures m_1–m_5.

trend (c.f. m_3 and m_5 in Fig. 2). On the other hand the results obtained for m_1 and m_4 in Figure 2 show that shifting the double bond from $1 \rightarrow 4$ causes k_{ii} to strongly decrease. Preliminary experiments performed with monotropic 2-alkenyls indicate that position 2 affects k_{ii} similarly to position 4. The positional dependent variations of k_{33} that follow from Figure 2 for pentyl alkenyls exceed 300%. To our knowledge such a broad k_{ii}-range has so far not even been reached when comparing markedly different polar LC-classes[1] such as pyrimidines, PCHs, esters, Schiff'bases, etc.

From Figure 2 follow two consequences which are important from a practical point of view as well as for a better understanding of structure-property relationships of nematics, namely: large variations of k_{33}/k_{11} and of $\kappa = k_{11} + (k_{33} - 2k_{22})/4$. This is shown in Figure 3 where the temperature dependences of k_{33}/k_{11} and of κ of mixtures m_1–m_5 are depicted. From Figure 3 follows that the elastic ratio k_{33}/k_{11} (i) increases when shifting the alkenyl double bond from $1 \rightarrow 3$ (c.f. m_1, m_2, m_3 and m_5) and (ii) decreases for a $1 \rightarrow 4$ shift (c.f. m_1 and m_4). Thus, for $T \ll T_c$ k_{33}/k_{11} varies between 1.5 and 3, i.e. by a factor of 2 (Fig. 3). The upper part of Figure 3 shows the analogous position-dependent behaviour of the elastic expression κ, i.e. κ increases by a factor of 2 when shifting the alkenyl double bond from positon $1 \rightarrow 3$ (c.f. m_1, m_3 and m_5).

Figure 4 shows the temperature dependence of the rotational viscosities γ_1 of mixtures m_1–m_5. From Figure 4 follows that $\gamma_1(T)$ can be qualitatively described at $T \ll T_c$ by

$$\gamma_1 \propto \exp(A/kT), \tag{1}$$

where A = activation energy. This finding agrees with $\gamma_1(T)$-measurements[7] as well as with measurements of the bulk viscosity[5] $\eta(T)$ made with other polar liquid crystals. Like the elastic constants, γ_1 also depends on the position of the alkenyl double bond. When disregarding for the moment differences of activation energies, Figure 4 shows that γ_1 increases when shifting the double bond from $1 \rightarrow 3$ (c.f. m_1 and m_3). Incorporating the ethane linkage into the rigid core causes γ_1 to increase still further (c.f. m_3 and m_5). On the other hand a shift from position $1 \rightarrow 4$ leads to a remarkable reduction of γ_1 (c.f. m_1 and m_4).

For a direct comparison of single components, Figure 5 shows the temperature dependence of the rotational viscosity of the two 1-position alkenyls $3d_1CP$ and $3d_1CAP$ as well as $\gamma_1(T)$ of the respective structurally related PCH5 and 5CAP. Also included in Figure 5 is K15.

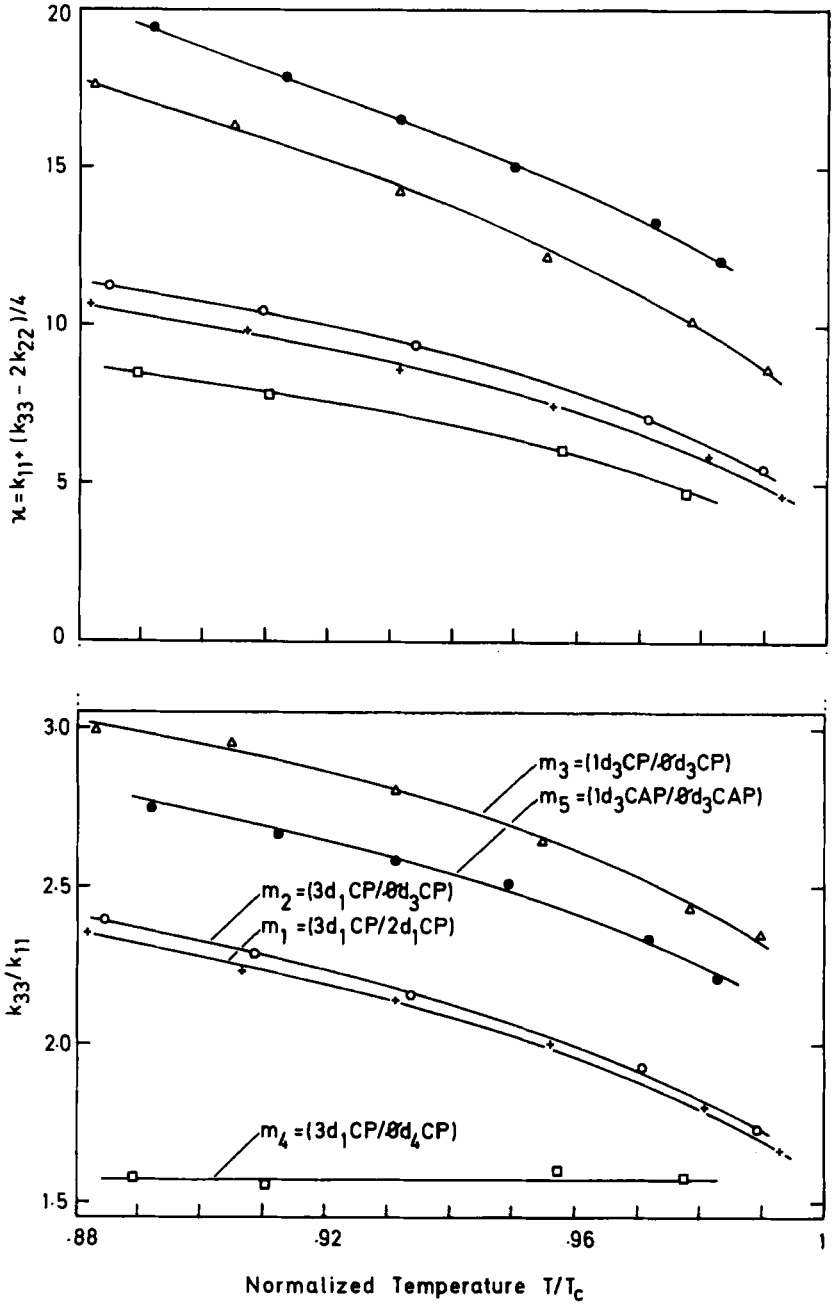


FIGURE 3 Temperature dependence of the elastic ratio k_{33}/k_{11} and of $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ of alkenyl mixtures m_1–m_5.

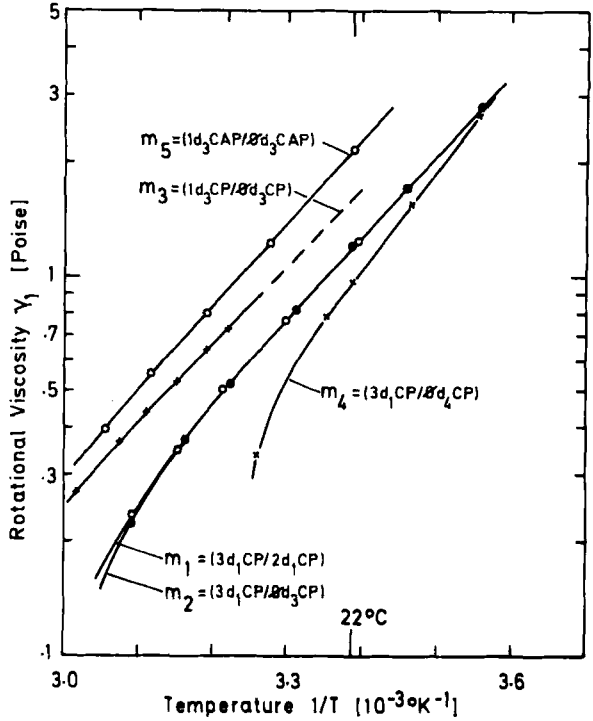


FIGURE 4 Temperature dependence of the rotational viscosities γ_1 of alkenyl mixtures m_1–m_5.

3. COMPARISONS BETWEEN ALKENYLS AND OTHER NEMATICS

3.1. LC-material parameters and electro-optical performance of TN-LCDs

The electro-optical measurements in TN-LCDs were made at vertical light incidence in $d = 8$ μm spaced, polymer aligned, low bias tilt, $\pi/4$-twisted displays. The LCD-response times were measured at driving voltages $V = 2.5\ V_{10}(T)$, where $V_{10}(T)$ = optical threshold voltage at temperature T corresponding to 10% transmission; t_{off} = decay time corresponding to a change of transmission from 100% $\rightarrow$ 10% following the turn-off of V.

From relating numerically calculated electro-optical characteristics with LC-material parameters and from the performance of materials in TN-LCDs we have shown earlier[1] that the slope of the transmission

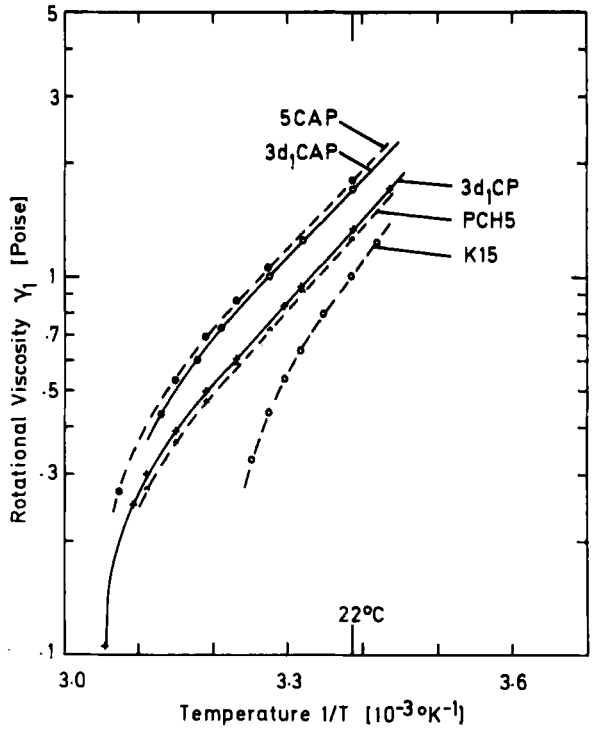


FIGURE 5 Temperature dependence of the rotational viscosities γ_1 of alkenyl components $3d_1CP$, $3d_1CAP$ and of reference compounds PCH5, 5CAP and K15.

characteristics of low bias tilt TN-LCDs can be approximated at vertical light incidence and around the second Mauguin transmission minimum by

$$p \simeq a + b\left(\frac{k_{33}}{k_{11}} - 1\right) + c\left(\ln \frac{\Delta nd}{2\lambda}\right)^2. \qquad (2)$$

The experimentally determined constants a, b and c depend on the specific TN-LCDs used i.e. on the technology such as the surface aligning technique. For our display $a = 0.119$, $b = 0.035$ and $c = 0.135$ hold. Approximation (2) shows that small elastic ratios k_{33}/k_{11} are most crucial for achieving small slope parameters $p = (V_{50} - V_{10})/V_{10}$ which—according to $N = [(p+1)^2 + 1)]^2/[(p+1)^2 -]^2$—are a prerequisite to reach large multiplexing ratios N. Other material parameters like k_{22}/k_{11} (which should be large to lower p)[15] and $\Delta\epsilon/\epsilon_\perp$ (which should be small in case of small optical path differ-

ences Δnd)[15] are—due to their minor importance at the second Mauguin minimum—neglected in (2).

Because of the increase of the select voltage with increasing multiplexing ratio, materials are required not only having steep electro-optical characteristics but also exhibiting optical thresholds low enough to remain CMOS-compatible. The optical threshold of TN-LCDs at vertical light incidence can be approximated by[1,16]

$$V_{10} \simeq V_{50}\left[0.88 - 0.024(k_{33}/k_{11} - 1) - 0.04\left(\ln \frac{\Delta nd}{2\lambda}\right)^2\right] \qquad (3)$$

where,

$$V_{50} = V_c\left[2.044 - 1.044/(k_{33}/k_{11} + 1)\right] \cdot\left[1 + 0.123\left\{(\Delta\epsilon/\epsilon_\perp)^{0.6} - 1\right\}\right]\cdot\left[1 + 0.132 \ln \frac{\Delta nd}{2\lambda}\right],$$

and the threshold for the mechanical deformation of the helical structure of the TN-LCD is

$$V_c = \pi\left[\kappa/\epsilon_0 \Delta\epsilon\right]^{1/2}.$$

From approximation (3) follows that both, the dielectric anisotropy $\Delta\epsilon$ as well as the elastic expression κ essentially determine V_{10} of TN-LCSD.

Because of the similar κ-values of the so far most frequently used polar nematics[1] it was often possible to relate directly the differences among different decay times of TN-LCDs to the different viscosities of the LC-materials. However, with compounds such as alkenyls exhibiting large κ-variations this approach leads to wrong conclusions about the dynamics of TN-LCDs. Thus, if complex numerical calculations such as those of Berreman[17] are avoided, at least the heuristic expression derived by Jakeman and Raynes[18] which relates small angles of deformations of the nematic director to the decay time t_d of TN-LCDs should be used:

$$t_d \propto \gamma/\kappa \qquad (4)$$

where γ is an undefined viscosity for which bulk viscosities η[5,6] and recently also rotational viscosities γ_1[7] were inserted. The small angle approximation (4) is not really applicable to the large director deformations corresponding to (practical) LCD turn-off times t_{off}[7]. All the

same it will be interesting to relate t_d of (4) qualitatively with γ_1, γ_1/κ and t_{off}.

3.2. Material properties and structures

Table II summarizes the material properties of the alkenyl components and mixtures of Table I as well as those of the reference compounds. Comparisons of the elastic, dielectric and optical properties are made at constant reduced temperature ($T_c - 10°C$), whereas viscosities and viscosity related properties are compared at $T = 22°C$ = constant. The data belonging to ($T_c - 10°C$) in Table II are depicted in the upper line of the respective compound; the lower line refers to 22°C.

Except for the optical anisotropy Δn and the mesomorphic temperature range which are both larger in case of $3d_1CP$, a comparison between the 1-alkenyl $3d_1CP$ and PCH5 shows that the two compounds are quite similar (Tab. I, II). Shifting the double bond from position $1 \rightarrow 3$ causes—in analogy to mixtures $m_1 \ldots m_5$—κ to increase strongly. Δn of $1d_3CP$ is about 30% larger than that of PCH5. The different Δn-values of $1d_3CP$ and $3d_1CP$ indicate that the angle of the double bonds parallel to the nematic director depends on bond position. From the data of the ethane linked components $3d_1CAP$ and 5CAP in Table II follows that the ethane linkage causes κ as well as k_{33}/k_{11} to increase compared with $3d_1CP$ and PCH5.

From the similar data of the dioxane mixtures m_6 and m_7 in Table II and from the data of $3d_1CP$ follows that the double bond in 1-position hardly affects the elastic or dielectric properties. However, in agreement with our earlier findings[1] the data of k_{33}/k_{11} of mixtures m_6 and m_1 show that heterocyclic rings in the rigid part of molecules lead to a reduction of k_{33}/k_{11}.

The striking dependence of k_{33}/k_{11} on alkenyl position led us to investigate semi-quantitatively whether rod-like and strain-free alkenyl conformations exist and whether the length/width ratio of the rods changes upon shifting the double bond. This was done with the Roche molecular modellings system (Roche Interactive Molecular Graphics RIMG)[20] designed to determine equilibrium structures and conformations of complex molecules based on inter- and intramolecular van der Waals interactions and conformational torsional potentials. To obtain the rod-like structures assumed by theory[9,10] we imposed the following boundary conditions: the strain-free conformations of the alkenyls have to fit into a cylindrically shaped frame in such a way that no unusual stress or strain bonding energies result.

TABLE II

Elastic constants $k_{11}, k_{22}, k_{33}, \kappa = k_{11} + (k_{33} - 2k_{22})/4$, static dielectric constants $\epsilon_\perp, \Delta\epsilon = (\epsilon_\parallel - \epsilon_\perp)$ and optical constants $n_0, \Delta n = (n_e - n_0)$ determined at the respective temperatures (T_c − 10°C) (upper lines) and T = 22°C (bottom lines). The dot in the bottom line of 5CAP indicates that the data are extrapolated to 22°C.

LC	k_{11}	k_{22}	k_{33}	k_3/k_1	κ	$\epsilon_\perp$	$\Delta\epsilon$	Δn	n_o
$3d_1$CP	6·22	3·90	13·4	2·13	7·5	5·70	10·94	0·116	1·490
	9·40	6·15	22·8	2·42	12·0	5·02	13·03	0·136	1·493
$1d_3$CP	9·41	5·74	24·1	2·56	12·6	5·02	13·13	0·130	1·483
$3d_1$CAP	9·18	5·28	18·5	2·02	11·2	4·96	10·48	0·118	1·486
	11·22	6·57	24·3	2·17	14·0	4·61	11·13	0·129	1·487
K15 (5B)	6·37	3·81	8·60	1·35	6·6	6·63	13·33	0·178	1·532
	7·12	4·09	9·82	1·38	7·5	6·46	13·82	0·185	1·533
PCH5 (5CP)	6·07	3·48	10·5	1·73	7·0	5·59	10·28	0·099	1·485
	8·98	4·73	18·3	2·03	11·2	4·85	12·22	0·119	1·487
5CAP	8·85	4·60	16·1	1·82	10·6	4·98	9·77	0·101	1·486
	• 12·05	6·65	24·0	1·99	14·7	4·40	10·80	0·116	1·483
m_1 = ($3d_1$CP/$2d_1$CP)	5·65	3·42	10·7	1·90	6·6	5·77	11·62	0·117	1·492
	7·83	4·75	17·4	2·22	9·8	5·20	13·89	0·138	1·494
m_2 = ($3d_1$CP/$\mathscr{B}d_3$CP)	6·10	3·92	11·8	1·93	7·1	5·56	11·49	0·115	1·493
	8·20	5·22	18·7	2·28	10·3	5·00	13·57	0·135	1·495
m_3 = ($1d_3$CP/$\mathscr{B}d_3$CP)	8·08	4·65	20·7	2·56	10·9	5·01	12·38	0·127	1·487
	12·29	6·80	36·5	2·97	18·0	4·40	15·10	0·153	1·493
m_4 = ($3d_1$CP/$\mathscr{B}d_4$CP)	4·90	2·80	7·50	1·53	5·4	6·18	10·80	0·105	1·498
	5·52	3·20	8·60	1·56	6·1	6·03	11·23	0·108	1·500
m_5 = ($1d_3$CAP/$\mathscr{B}d_3$CAP)	10·25	5·95	24·3	2·37	13·4	4·64	11·74	0·122	1·485
	13·80	8·00	37·9	2·75	19·3	4·17	13·37	0·139	1·486
m_6 = ($4d_1$DP/$3d_1$DP)	4·80	3·00	6·14	1·28	4·8	9·75	15·62	0·099	1·491
m_7 = (4DP/5DP)	4·73	3·08	6·43	1·36	4·8	10·58	15·27	0·089	1·488
	5·88	3·99	8·41	1·43	6·0	9·99	17·06	0·100	1·487

The cylindrical frame was defined by the rod-shaped van der Waals volume resulting from the rotation of a tricyclic bicyclooctane structure around its long axis. At one end of the cylinder a benzene ring was attached which had favourably to coincide with the benzene ring P of the alkenyl fitted into the cylinder.

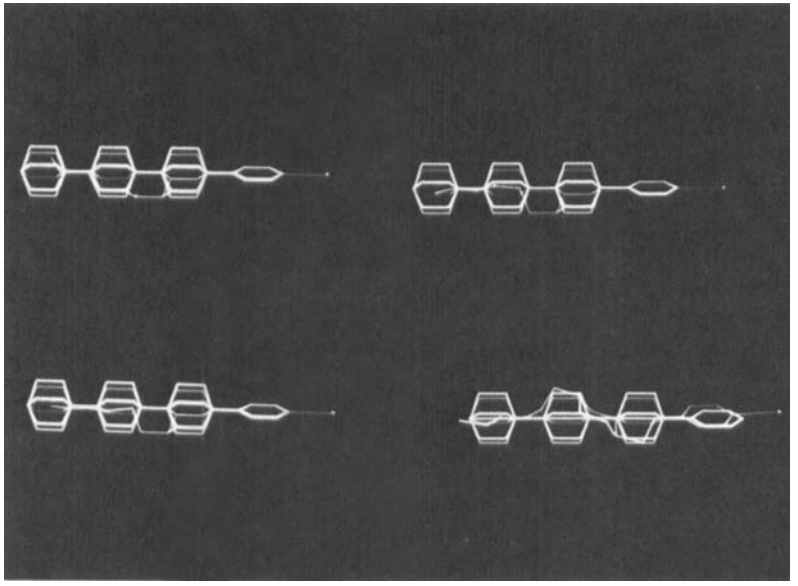


FIGURE 6 Energetically relaxed molecular conformations of polar alkenyls (red structures) fitted by molecular modelling into a cylindrically shaped bicyclooctane frame (blue-white structure) to which a benzene ring is attached on the right. The following alkenyls are fitted into the frame $4d_1CP$ (upper left), $2d_3CP$ (upper right), $1d_4CP$ (lower left) and $2d_3CAP$ (lower right). See Color Plate IX located in the final volume of these Conference Proceedings.

Figure 6 shows the calculated equilibrium structures of $4d_1CP$, $2d_3CP$, $1d_4CP$ and $2d_3CAP$ (red molecules) in the rotationally symmetric bicyclooctane cylinder. The position of the alkenyl double bond is indicated with two red dots, the cyano end group pointing to the right (red dot connected to benzene ring). From Figure 6 follows that even the bulky ethane-linked alkenyl $2d_3CAP$ fits well into the cylinder if a dislocation of its benzene ring from the benzene ring of the frame is allowed. The resulting strain-free conformations in Fig. 6 show that the length/width ratios of the directly linked alkenyls are—independently of the position of the double bond—identical, i.e. L/W = constant. Therefore, we see no reason to relate the constant length/width ratio L/W of alkenyls with the strongly different elastic ratios $1.5 < k_{33}/k_{11} < 2.6$ of $3d_1CP$, $1d_3CP$ and m_4 (Table II). Besides, although L/W of the rod formed by $1d_3CAP$ increases due to the ethane linkage its k_{33}/k_{11} does not increase (Tab. II).

By analogy to the above, Figure 7 shows the long and short axis of the rod-shaped van der Waals radii of the strain-free conformation of

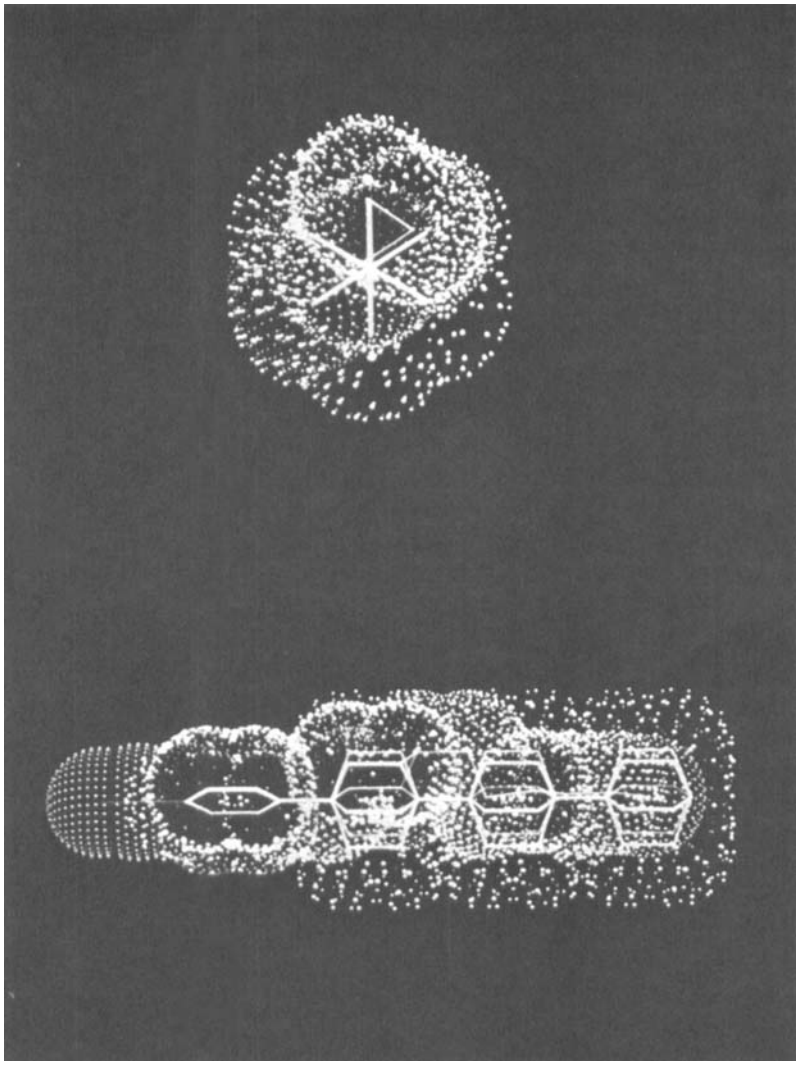


FIGURE 7 van der Waals radii of bicyclooctane cylinder frame (blue-white dots) incorporating $2d_3CP$ (red dots). The lower picture shows the rod-shaped long cylinder axis whereas the upper part is a projection of the alkenyl side chain along the long cylinder axis showing its fit into the bicyclooctane frame. See Color Plate X located in the final volume of these Conference Proceedings.

$2d_3CP$ of Figure 6 within the bicyclooctane frame. Figure 7 shows that the rod-like van der Waals shapes of polar alkenyls indeed fit well into the cylindrically shaped bicyclooctane van der Waals frame.

3.3. The dynamics of alkenyls

From the rotational viscosities depicted in Figures 4 and 5 one would expect 1,4-alkenyl mixture m_4 to exhibit a faster electro-optical reponse than either PCH5 or the 3-alkenyl mixture m_3. However, their visco-elastic ratios $\alpha = \gamma_1/\kappa$ depicted in Figure 8 indicate that this is not the case. Figure 8 shows that not only the course of the temperature dependence of γ_1/κ changes compared with γ_1 (Fig. 4) but also the respective order of increasing γ_1 and γ_1/κ. Thus, although $\gamma_1(m_4) < \gamma_1(PCH5) < \gamma_1(m_3)$ it follows from the κ-values of Figure 3 that $\gamma_1/\kappa(m_4) > \gamma_1/\kappa(PCH5) > \gamma_1/\kappa(m_3)$. Therefore, and provided approximation (4) holds, m_3 is expected to exhibit considerably faster decay times than the less viscous mixture m_4 or PCH5.

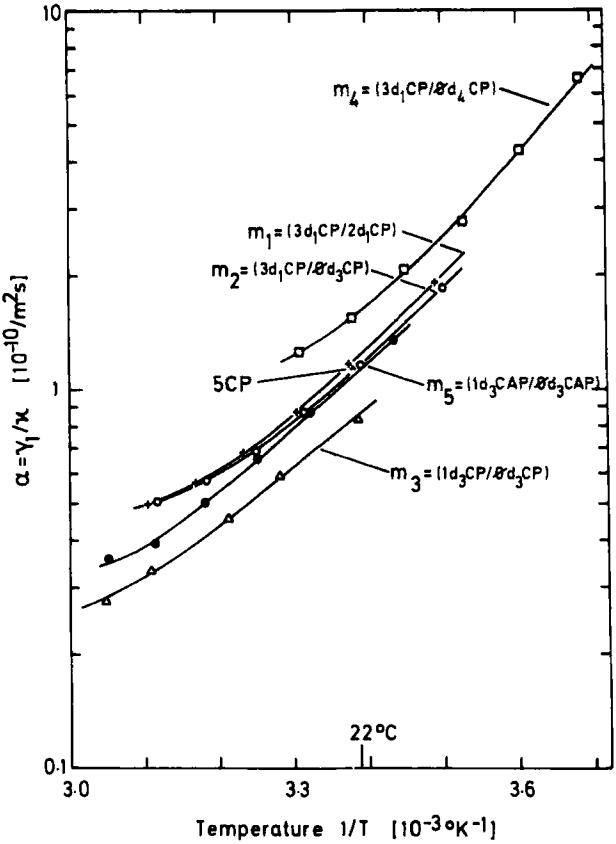


FIGURE 8 Temperature dependence of the visco-elastic ratio γ_1/κ of alkenyl mixtures m_1–m_5. Also included is PCH5 (5CP).

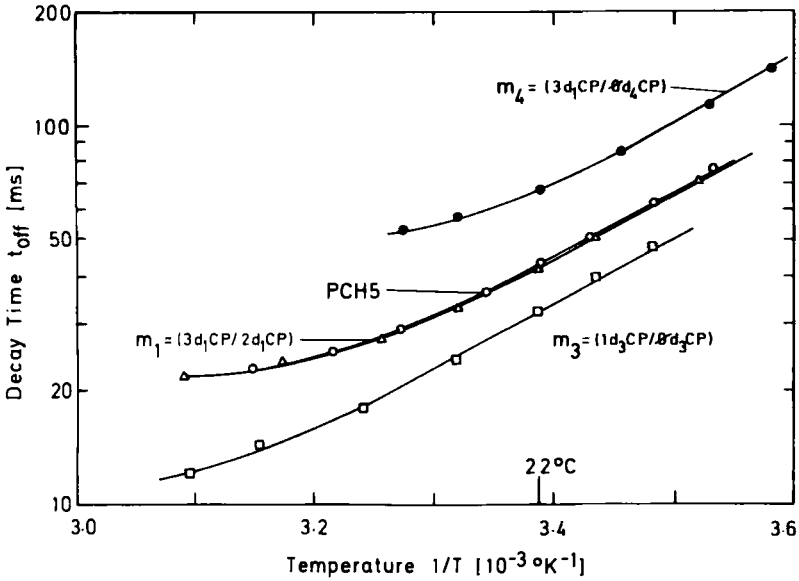


FIGURE 9 Temperature dependence of the decay time t_{off} of TN-LCDs comprising alkenyl mixtures m_1, m_3, m_4 and PCH5 respectively.

Figure 9 shows that the activation energies of the decay times $A(t_{off})$ at $T \ll T_c$ are comparable to those of the visco-elastic ratios $A(\gamma_1/\kappa)$ of Figure 8 but smaller than $A(\gamma_1)$. The data are summarized in Table III.

Moreover, the order of increasing t_{off} is the same as that found for γ_1/κ (Fig. 8 and 9). Thus, the simple approximation (4) can be used—together with γ_1/κ—to predict qualitatively the decay times of TN-LCDs at least over the rather small temperature ranges investigated here.

TABLE III

Activation energies A of the rotational viscosity γ_1, the visco-elastic ratio γ_1/κ and the TN-LCD decay time t_{off} (100% → 10%) at $T \ll T_c$.

	$A(\gamma_1)$ [eV]	$A(\gamma_1/\kappa)$ [eV]	$A(t_{off})$ [eV]
m_4	0.51	0.39	0.36
m_1	0.42	0.35	0.32
PCH5	0.43	0.35	0.32
m_3	0.41	0.32	0.32

TABLE IV

Rotational (γ_1) and bulk viscosities (η), activation energy $A(\gamma_1)$ of γ_1, visco-elastic ratio $\alpha = \gamma_1/\kappa$ as well as normalized visco-elastic ratios $\alpha(LC)/\alpha(5CP)$ and TN-LCD decay times $t_{off}(LC)/t_{off}(5CP)$ normalized with respect to PCH5. V_{10} = optical threshold voltage of TN-LCDs. All measurements made at 22°C.

LC	γ_1 [Poise]	$A(\gamma_1)$ [eV]	$\alpha = \frac{\gamma_1}{\kappa}$ [10^{-10}/m^{2}s]	$\frac{\alpha(LC)}{\alpha(5CP)}$	η [Poise]	t_{off} [ms]	$\frac{t_{off}(LC)}{t_{off}(5CP)}$	V_{10} [Volts]
$3d_1CP$	1·34	·43	1·11	·97	·221	40	·93	1·58
$3d_1CAP$	1·70	·41	1·21	1·06	·228	38	·88	1·89
K15 (5B)	1·01	54	1·35	1·18	·263	55	1·28	1·13
PCH5 (5CP)	1·28	·43	1·14	1·00	·215	43	1·00	1·55
5CAP	1·80	·42	1·22	1·07	·224	43	1·00	2·00
$m_1 = (3d_1CP/2d_1CP)$	1·21	·42	1·23	1·08	·228	42	·98	1·47
$m_2 = (3d_1CP/3d_3CP)$	1·19	·42	1·15	1·01	·209	37	·86	1·62
$m_3 = (1d_3CP/3d_3CP)$	1·50	·41	·83	·73	·190	32	·74	2·09
$m_4 = (3d_1CP/3d_4CP)$	·97	·51	1·59	1·38	·278	67	1·56	1·13
$m_5 = (1d_3CAP/3d_3CAP)$	2·15	·43	1·11	·98	-	29	·67	2·29

Table IV shows measurements made at 22°C of the rotational and bulk viscosities γ_1 and η of alkenyls and reference compounds. Also shown are their activation energies $A(\gamma_1)$, the viscoelastic ratios, the decay times and the optical threshold voltages. Because of their comparable dielectric anisotropies (Tab. II) and in agreement with approximation (3), the compounds with large κ-values also exhibit high optical thresholds V_{10} (Tab. IV). Table IV shows that γ_1 of m_4 and K15 are considerably lower than those of m_3 or PCH5. However, the decay times of m_4 and K15 are—due to their large visco-elastic ratios—more than 30% larger than t_{off} (PCH5). On the other hand the response of the 3-alkenyl mixture m_3 is 26% faster than that of PCH5 (Tab. IV, Fig. 9). From the κ-values in Table II and the bulk viscosities η depicted in Table IV follows that η/κ and t_{off} correlate not as well as γ_1/κ and t_{off}. The discrepancy becomes most pronounced when comparing the low γ_1 compounds K15 and m_4 with the other compounds in Table IV. This finding confirms our earlier results obtained with other LC-classes[7]. From the above follows that even qualitative electro-optical response considerations cannot be based on viscosity data alone, the elastic properties must be considered too.

4. CONCLUSIONS

From investigations into the dielectric, birefringence, viscous, electro-optical and all three elastic constants we have shown that the new, low viscous polar nematic alkenyls synthesized in our laboratories cover an unusually wide range of elastic properties rendering them applicable in LCDs requiring fast response as well as high multiplexability. With sterically and dielectrically comparable representatives of five different alkenyl classes it was found that the elastic ratio k_{33}/k_{11} as well as the elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ strongly depend on the position of the alkenyl double bond in the hydrocarbon side chain. By means of molecular modelling, the rod-like van der Waals structure of directly—as well as ethane linked alkenyls was verified and shown that the length/width ratio L/W of the rods is constant. On the other hand $k_{33}/k_{11} \neq$ constant. Therefore, and since steric considerations alone do not suggest the postulation of hypothetical steric units either whose L/W-ratio may (or may not) change, we conclude that hard-rod models that disregard specific molecular interactions and which imply $L/W \propto k_{33}/k_{11}$ are inade-

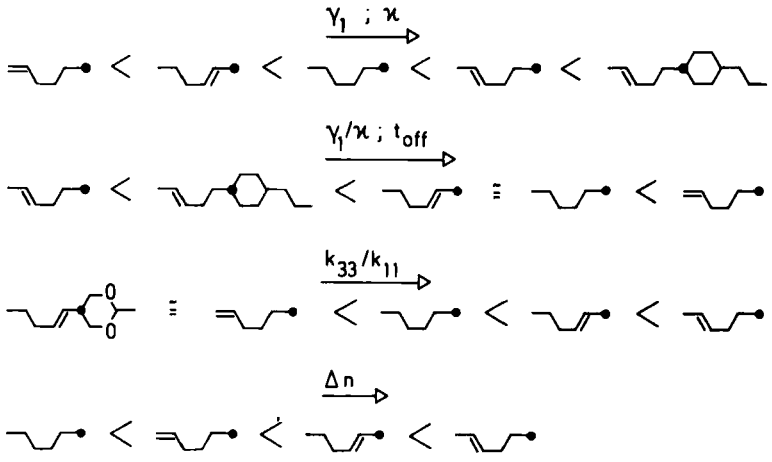


TABLE V

Summary and schematic representation of the influence of alkenyl double bond position on γ_1, κ, γ_1/κ, t_{off}, k_{33}/k_{11} and Δn. Directly linked alkenyls with PCH-core are depicted with their alkenyl side chains only. In case of the ethane-linked (ld_3CAP) and the dioxane ($3d_1$DP) alkenyl, the rings attached to the alkenyl side chain are included. Also included in the schematic is PCH5 (saturated chain).

quate to describe the elastic ratios of nematics. Because of the low rotational viscosities and the large κ-values of 3-alkenyls, low visco-elastic ratios γ_1/κ result. As a consequence, 3-alkenyls exhibit response times in TN-LCDs that are ~30% shorter than those of comparable PCHs while their optical anisotropy Δn is larger than Δn of PCHs. By analogy with our earlier findings with other liquid crystal classes, rigid cores of alkenyls comprising heterocyclic rings are shown to exhibit lower elastic ratios k_{33}/k_{11} than non-heterocyclic compounds.

Table V summarizes schematically our findings of the positional-dependent influence of the alkenyl double bond on k_{33}/k_{11}, κ, γ_1, γ_1/κ and Δn. Also shown is the influence of the dioxane ring on k_{33}/k_{11} and the effect of the ethane linkage in the 'rigid' core. Due to the dependence of Δn on double bond position, the average angle of the bond with respect to the nematic director is—contrary to the schematic in Table V—position dependent.

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