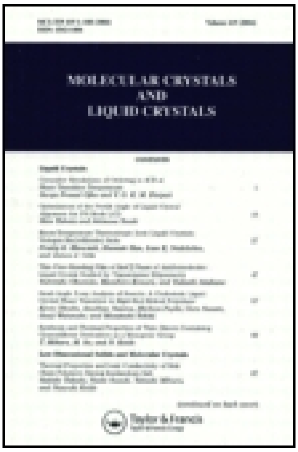

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Synthesis, Physical Properties and Structural Relationships of New, End-Chain Substituted Nematic Liquid Crystals

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Synthesis, Physical Properties and Structural Relationships of New, End-Chain Substituted Nematic Liquid Crystals†

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New nematic liquid crystalline phenylcyclohexanes with (i) a terminal side-chain vinylic group some distance from the rigid core and (ii) both polar and non-polar terminal side-chain groups, were synthesized.

Investigations of their elastic, birefringence, dielectric and rotational viscous properties have shown several new odd–even effects. These are attributed to side-chain position-dependent induced dipole–dipole interactions of the alkenyl double bonds. Simultaneous odd–even effects were found for $\Delta\varepsilon$, Δn, k_{33}/k_{11} and $\kappa = k_{11} + (k_{33} - 2k_{22})/4$. Furthermore, unusually low twist elastic constants, k_{22} were obtained for polar 6-alkenyls as well as for compounds exhibiting groups with permanent dipole moments in even side-chain positions.

Keywords: nematic mesogens, odd/even effects, vinyl groups

1. INTRODUCTION

Recently we have shown that incorporation of a Z- or E-double bond into side-chains of nematic liquid crystal molecules, leads to remarkable changes in their mesomorphic, elastic, viscous and electro-optical properties.[1–5] Thus, 1(E)- and 3(E)-alkenyls exhibit broader mesophase ranges and considerably larger bend/splay elastic ratios k_{33}/k_{11} than their saturated analogues, whereas the opposite holds true for

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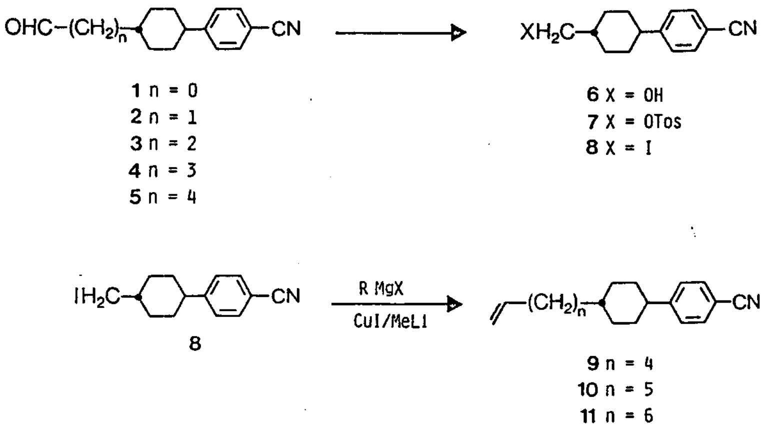
4(E)-alkenyls. The specific properties of alkenyls were attributed to the position-dependent influence of the π-electrons of the alkenyl group, leading to position-dependent changes of induced dipole–dipole interactions between molecules.[1]

A number of questions arose from our previous work—such as to what extent would alkenylation at side-chain positions farther away from the rigid core than C(4) affect the physical properties of alkenyls. Furthermore, would replacement of the alkenyl group by similar π-electron containing groups, such as acetylenes or allenes lead to similar material properties? Since not only distributed induced dipole moments, but also permanent dipole moments in side-chains of liquid crystals may affect their properties, the question arises: whether, and to what extent, a similar effect occurs when replacing alkenyl groups by polar terminal groups such as halogen, aldehyde or cyano.

In the following account, the synthesis and properties of a number of new mesogens are described with (i) terminal alkenyl groups in C(5), C(6) and C(7) position; with (ii) acetylene or allene terminal groups, as well as with (iii) terminal halogen, aldehyde or cyano groups. Their synthesis and physical properties will be described and comparisons will be made between the new compounds and both their saturated and their shorter alkenyl counterparts with double bonds in C(3) and C(4) position.

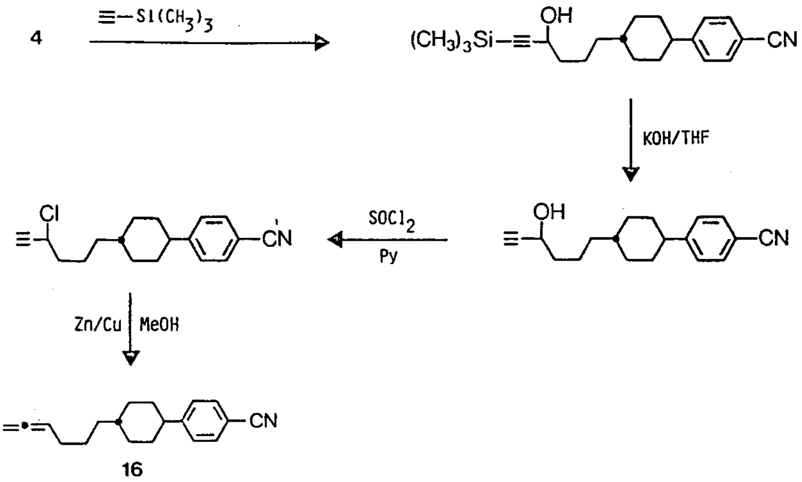
2. SYNTHESIS

In our previous syntheses of liquid crystalline phenylcyclohexanes with Δ1 to Δ4-alkenyl side-chains, the bifunctional cyanoaldehyde 1 was used as a key compound.[2] Homologous aldehydes (2–4) were prepared by stepwise chain elongation. From these aldehydes the corresponding alkenyls were prepared by Wittig olefination. To follow this synthetic route for preparing the alkenyls considered here (with the olefinic group farther removed from the rigid core than C(4)) would require a large number of steps. Therefore, a one step introduction of the desired side-chain into a suitable key compound like 7 or 8 was attempted. These key compounds are easily prepared from cyanoaldehyde 1 via the alcohol 2. Different attempts to introduce the side-chain by a conventional Fouquet–Schlosser reaction[6] were not successful. However, a modified application of a mixed methyl cuprate[7] led to the desired terminal alkenyl compounds in high yields. The corresponding methyl-coupling could be suppressed down to 5 percent. From the resulting nitriles, isothiocyanates were prepared according to known methods.[8]



SCHEME I

The synthesis of the allenic compound 16 was made according to Scheme 2.



SCHEME II

The carbon/silicon bond was cleaved by KOH. Chlorine substitution and reduction to the allene were preformed according to Ref. 9.

The terminal acetylenes 17–19 were prepared by standard methods starting with the homologous aldehydes 3–5, Wittig reaction with $Br_2CH_2PPh_3$ Br and subsequent elimination/reduction with butyllithium. Also the terminally substituted halogenides 20–23 and 26 and the nitrile 25 were readily prepared by reduction of the corresponding aldehydes 4 and 5 to 24 and 27 respectively, and by subsequent tosylation and Finkelstein reaction.

3. RESULTS AND DISCUSSION OF MESOMORPHIC PROPERTIES

3.1. Δ5–Δ7 Vinylic phenylcyclohexanes

The thermoanalytical data are shown in Table I. For comparison, previously published data of alkenyl homologues and saturated analogues are included. It is apparent in Table I that alkenylation of the nitriles not only at C(1) and C(3)[2] but also at C(5) leads to broader mesophase ranges than for the saturated compounds. The Δ7-alkenyl compound is exceptional and this tendency does not occur. In the isothiocyanate series (Table I) the same tendency was found for the Δ7-alkenyl although the difference here is very small. The distinct broadening of the mesorange towards lower temperatures is observed for terminally alkenylated isothiocyanates, whilst in the nitrile series the mesorange shift was found to systematically alternate compared with the saturated compounds (Table I).

3.2. Terminal acetylenes and allenes

With one exception[10] the influence of the acetylenic group on the mesomorphic properties of LC's has been previously investigated only for compounds where this group was either part of the rigid core or attached close to it. To study its influence when part of the side-chain, we synthesized three homologous terminal acetylenes and one terminal allene. The thermodynamic data of the four new compounds are listed in Table II.

From Table II it is apparent that, in contrast to alkenylation, the introduction of a terminal acetylene group largely destroys the liquid crystalline properties. This occurs regardless of chain-length. The same tendency, although to a lesser extent, was found with the allene (Table II). However, both of its new LC-classes exhibit melting tem-

TABLE I

Mesomorphic properties of terminal alkenyls compared to the those of the corresponding saturated compounds.

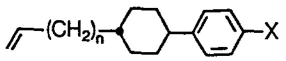
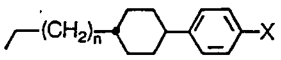
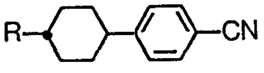
<table>
<tr><td colspan="8"></td><td colspan="4"></td></tr>
<tr><th>No</th><th>n</th><th>X</th><th>T_m</th><th>T_c</th><th>T_c-T_m</th><th>ΔH</th><th>Lit.</th><th>T_m</th><th>T_c</th><th>T_c-T_m</th><th>Lit.</th></tr>
<tr><td></td><td>0</td><td>CN</td><td>56.4</td><td>(28.5)</td><td>-27.9</td><td>4.15</td><td>2</td><td>40</td><td>(4)</td><td>-36</td><td>11</td></tr>
<tr><td></td><td>1</td><td></td><td>29.2</td><td>[-30.5]</td><td>-59.7</td><td>5.11</td><td>2</td><td>36</td><td>46</td><td>10</td><td>11</td></tr>
<tr><td></td><td>2</td><td></td><td>49.5</td><td>52.5</td><td>3.0</td><td>3.63</td><td>2</td><td>41</td><td>41</td><td>0</td><td>11</td></tr>
<tr><td></td><td>3</td><td></td><td>29.8</td><td>(10.2)</td><td>-19.6</td><td>5.29</td><td>2</td><td>31</td><td>55</td><td>14</td><td>11</td></tr>
<tr><td>9</td><td>4</td><td></td><td>45.5</td><td>52.5</td><td>7.0</td><td>6.43</td><td></td><td>42</td><td>47</td><td>5</td><td>11</td></tr>
<tr><td>10</td><td>5</td><td></td><td>19.2</td><td>32.3</td><td>13.1</td><td>5.44</td><td></td><td>30</td><td>59</td><td>29</td><td>11</td></tr>
<tr><td>11</td><td>6</td><td></td><td>38.0</td><td>53.2</td><td>15.2</td><td>7.64</td><td></td><td>33</td><td>54</td><td>21</td><td>11</td></tr>
<tr><td></td><td>2</td><td>NCS</td><td>24.6</td><td>43.7</td><td>19.1</td><td>2.53</td><td>4</td><td>34.5</td><td>(32.0)</td><td>-2.5</td><td>8</td></tr>
<tr><td>12</td><td>3</td><td></td><td>38.8</td><td>[-10]</td><td>-48.8</td><td>6.20</td><td></td><td>67.5</td><td>(49.5)</td><td>-18.0</td><td>8</td></tr>
<tr><td>13</td><td>4</td><td></td><td>15.2</td><td>46.1</td><td>30.9</td><td>3.65</td><td></td><td>12.5</td><td>43.0</td><td>30.5</td><td>8</td></tr>
<tr><td>14</td><td>5</td><td></td><td>1.6</td><td>19.0</td><td>17.4</td><td>3.79</td><td></td><td>37.0</td><td>52.0</td><td>15</td><td>8</td></tr>
<tr><td>15</td><td>6</td><td></td><td>24.6</td><td>45.5</td><td>20.9</td><td>6.43</td><td></td><td>28.0</td><td>48.0</td><td>20</td><td>8</td></tr>
</table>

TABLE II

Mesomorphic properties of phenylcyclohexanes with acetylene and allene group as terminal substituents



No	R	T_m	T_c	T_c-T_m	ΔH
17		139	[42.5]	-96.5	6.26
18		86.2	[1.5]	-84.7	7.51
19		112.1	[56.1]	-56	6.29
16		44.7	[-1.5]	-46.2	6.68

peratures which are clearly higher than those of analogous saturated or vinyl series.

3.3. Terminal polar substituents

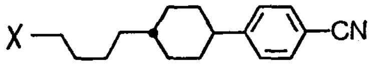
So far we have investigated only the influence of different induced dipole moments in terminal position on the mesomorphic properties of liquid crystals. Polar terminal substituents, i.e., substituents exhibiting permanent dipole moments, have not yet been considered.

Table III shows the thermodynamic data of a number of new liquid crystalline compounds with different terminal polar groups. From Table III it is apparent that halogenation has a strongly detrimental effect on the mesomorphic temperature range, with fluorine being least damaging. On the other hand, the introduction of a terminal hydroxyl group leads (probably due to dimer formation) to broader mesophase ranges (cf. C_4 and C_5 in Table III).

Table III also shows that a terminal aldehyde group leads (depending on its position) either to an enhanced mesomorphic range

TABLE III

Mesomorphic properties of phenylcyclohexanes with polar substituents at the ends of the side-chains.



No	X	T_m	T_c	T_c-T_m	ΔH
20	F	42.6	(33.7)	-8.9	6.32
21	Cl	64.9	(31.0)	-33.9	6.00
22	Br	63.5	[42.9]	-20.6	5.74
23	I	71.0	[42.1]	-28.9	4.56
24	HO	79.1	89.6	10.5	5.86
4	=O	55.5	(43.6)	-11.9	5.87
25	CN	76.5	44.0	-32.5	5.88
26	CH_2Cl	39.6	(38.0)	-1.6	6.84
27	CH_2OH	91.1	103.9	12.8	3.69
5	HC=O	36.0	53.0	17.0	4.76

(cf. C(5)-aldehyde), or to a strongly depressed (monotropic) range (cf. C(4)-aldehyde) compared with the analogous saturated compounds in Table I. This alternating, position-dependent behaviour is similar to that found in alkenyls (Table I). Finally, Table III shows that the introduction of a terminal nitrile group has an effect on mesophase formation similar to halogenation.

When comparing a particular terminal polar group attached at different chain lengths (Table III), it is interesting to note that both the chlorinated and the hydrogenated compounds with five side-chain carbon atoms, exhibit broader mesophase ranges than those with four carbon atoms. If we count the heteroatom as a side-chain carbon atom, then, this observation corresponds to an *inverse* odd–even effect.

4. PHYSICAL PROPERTIES AND STRUCTURAL RELATIONS

4.1. CN- and NCS-alkenyls

We have previously shown that both polar[1,4] and non-polar[5] 1- to 4-position alkenyls make available an exceptionally wide range of elastic properties giving compounds suitable for liquid crystal displays (LCDs) requiring fast response as well as high multiplexibility.[3,4] Thus, cyano 1- and 3-alkenyls exhibit large bend/splay elastic ratios k_{33}/k_{11},[1] reaching $k_{33}/k_{11} = 3$ at (T_c − 10°C), whereas ratios as low as $k_{33}/k_{11} = 0.5$ were achieved with 4-position alkenyls.[4,5] The value of $\kappa = [k_{11} + (k_{33} - 2k_{22})/4]$, which determines, together with the dielectric anisotropy $\Delta\varepsilon$ ($\varepsilon_{\parallel} - \varepsilon_{\perp}$), the threshold voltage $V_{10} \propto (\Delta\varepsilon/\kappa)^{1/2}$ [12] of twisted nematic TN–LCs, was found to alternate among 1-, 3- and 4-alkenyls[1] in a similar fashion to k_{33}/k_{11} but in a less pronounced manner.

Figure 1 shows the temperature-dependence of the elastic ratio k_{33}/k_{11} of three NCS- and two CN-alkenyls with the double bond at different terminal side-chain positions far removed from the rigid core. In Figure 1 and Table IV the same nomenclature is used as before[1,5] that is, d_i = double bond, where the index designates its position from C; C = cyclohexane ring; P = phenyl ring; S = NCS group. The number following d_i indicates the number of carbon atoms following the double bond. For comparison the 3-alkenyl $2d_3CPS$[4] exhibiting the same number of side-chain carbon atoms as ϕd_5CPS is included in Figure 1.

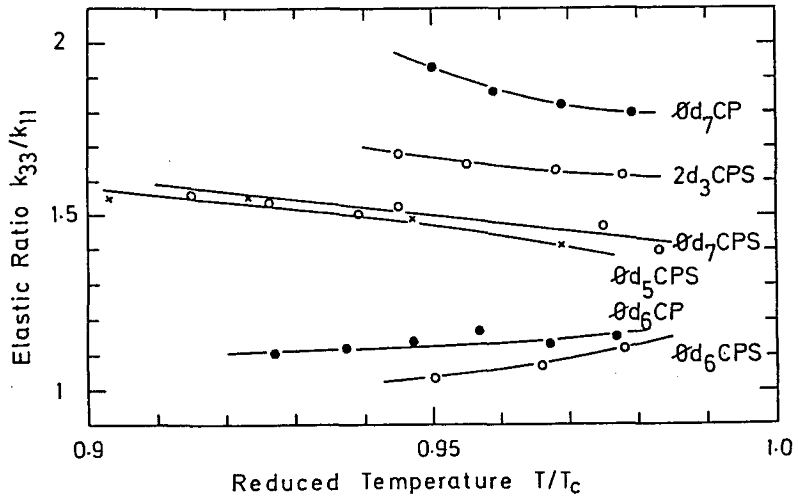


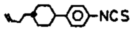
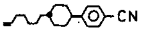
FIGURE 1 Temperature dependence of the splay/bend elastic ratio k_{33}/k_{11} of polar alkenyls. The nomenclature used is described in the first two rows of Table IV.

From Figure 1 and the elastic data in Table IV it is apparent that the alkenyl position-dependent alternation of k_{33}/k_{11} holds not only for 1-, 2-, 3- and 4-alkenyls as found before,[1,4] but also for alkenyl positions farther away from the rigid core. Thus, an elastic odd–even effect can be formulated, such that odd alkenyl positions d_1, d_3, d_5 d_7, etc. lead to large bend/splay elastic ratios, whereas even positions (d_2, d_4, d_6, etc.) strongly reduce this ratio. Moreover, from our investigations into non-polar alkenyls with alkenyloxy side-chains[5] it was found that the same odd–even effect also occurs for alkenyloxy side-chains. Analogous to our earlier findings,[4] Figure 1 confirms that replacement of the cyano end group by NCS leads to a reduction of k_{33}/k_{11} (cf. ϕd_7CP, ϕd_7CPS and ϕd_6CP, ϕd_6CPS in Table IV).

Table IV shows the optical, dielectric and elastic properties of the new cyano and NCS alkenyls determined at their reduced temperatures ($T_c - 10°C$). The rotational viscosity γ_1 was measured at constant temperature T = 22°C. The saturated NCS compound 6CPS[9] and the homologues ϕd_3CPS and $2d_3CPS$[4] are also included in Table IV. It is interesting to note that ϕd_6CPS not only exhibits a low bend/splay elastic ratio but also a twist elastic constant $k_{22} = 2.11$ which to our knowledge, is the lowest value reported for nematics so far. From Table IV it is also apparent that the optical (Δn) and the dielectric ($\Delta\varepsilon$) anisotropies of compounds with uneven alkenyl po-

TABLE IV

Birefringence $\Delta n = (n_e - n_o)$; dielectric anisotropy $\Delta\varepsilon = (\varepsilon_\parallel - \varepsilon_\perp)$; elastic constants k_{11}, k_{22} in $[\times 10^{-12}\mathrm{N}]$; elastic ratio k_{33}/k_{11}; elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ in $[\times 10^{-12}N]$ and rotational viscosity γ_1 in $[cP]$ of NCS- and CN-alkenyls. Except for γ_1, the measurements were made at $(T_c - 10°C)$ = constant.

Structure	Nomencl.	T_m	T_c	n_o	Δn	$\varepsilon_\perp$	$\Delta\varepsilon$	k_{11}	k_{22}	k_3/k_1	κ	γ_1
	ϕd_3CPS	25	43.1	1.530	0.183	4.12	8.60	7.73	4.30	2.00	9.5	51
 ··	2d_3CPS	24	35.9	1.526	0.166	4.00	8.32	7.70	3.20	1.64	9.3	97
 ··	ϕd_5CPS	15	46.5	1.524	0.157	3.90	6.75	8.02	3.49	1.41	9.1	95
 ··	ϕd_6CPS	2	19.8	1.537	0.130	5.07	5.63	4.65	2.11	1.07	4.8	-
 ··	ϕd_7CPS	24	45.5	1.520	0.144	3.85	6.20	6.77	3.39	1.47	7.6	-
 ··	6CPS	13	42.8	1.521	0.137	4.30	6.91	6.71	2.93	1.10	7.1	83
	ϕd_6CP	19	32.2	1.501	0.086	5.90	8.41	4.79	2.51	1.14	4.9	99
 ··	ϕd_7CP	38	52.9	1.501	0.099	5.00	9.40	7.25	3.81	1.83	8.6	-
		measured at: $(T_c - 10°C)$										22°C

sitions are larger than those with even positions or saturated side-chains. Thus, Δn of ϕd_3CPS even surpasses Δn of the cyano biphenyl K15,[12] despite the hydrogenated ring in the rigid core of the former. The rather large optical anisotropies of NCS-compounds compared with CN-compounds (Table IV) are a result of the extended conjugated π-electron system of the NCS-group. The alkenyl position dependent odd–even effect for Δn and $\Delta\varepsilon$ shown in Table IV agrees with our earlier findings for short side-chain CN-alkenyls. In these studies we showed, by means of an interactive molecular graphics technique, that the equilibrium side-chain structures of alkenyls vary strongly with the position of the double bond.[1] As a result, the projection of the π-electrons of the double bond into the direction of the nematic director alternates with alkenyl position and so do Δn and $\Delta\varepsilon$.

From the exceptionally low rotational viscosity γ_1 of ϕd_3DPS and its large elastic expression κ (Table IV), low visco-elastic ratios γ_1/κ and therefore short electro-optical response times can be expected.[1,4] From $\gamma_1(2d_3\mathrm{CPS}) \simeq \gamma_1(\phi d_5\mathrm{CPS})$ in Table IV and reference[3] it follows that the rotational viscosity is independent of alkenyl position, provided equally long side-chains are compared and the alkenyl positions are either even or odd only.

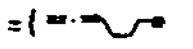
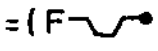
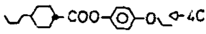
4.2. Acetylenes, allenes and polar terminal groups

Recently we have shown[4] that the rotational viscosity of CN-compounds decreases upon replacing the cyano by NCS and/or by introducing a double bond into 4-position of an alkyl side-chain.[3] On the other hand, shifting the alkenyl group into the 3-position was found to increase γ_1.[3] In the following account we will show to what extent the terminal substituents depicted in Table V affect the rotational viscosity. Except for ϕd_6CPS, identical overall side-chain lengths were used. Since all of these terminally substituted compounds are monotropic, binary mixtures were made together with the non-polar, low viscous ester 4CEPO2,[13] whose material properties were determined and are included for comparison at the bottom of Table V. A constant molar proportion of 1:1 was chosen for mixtures M1–M5 (Table V).

Figure 2 shows the temperature dependence of the rotational viscosity γ_1 of the single components 4CEPO2, ϕd_6CP and of the binary mixtures M1–M4. Figure 2 shows that the terminally fluorinated compound induces the smallest γ_1-depression (cf. 4CEPO2 and M3), whereas the two low viscous alkenyls ϕd_4CP (M1) and ϕd_6CPS (M4) lead to the strongest reduction of γ_1. It is interesting to note that

TABLE V

Physical properties of phenylcyclohexanes with different terminal substituents determined in binary mixtures M1–M5 (molar proportions 1:1).

Mixture (50%mol/50%)	T_m	T_c	n_o	Δn	$\varepsilon_\perp$	$\Delta\varepsilon$	k_{11}	k_{22}	k_3/k_1	$\varkappa$	γ_1
M1 = ( CN, 4CEPO2)	3	40.2	1.492	0.069	5.71	4.16	4.11	2.28	1.14	4.1	70
M2 = ( " ,4CEPO2)	2	29.5	1.504	0.072	6.00	4.52	4.14	2.42	1.19	4.2	68
M3 = (F  " ,4CEPO2)	2	48.3	1.485	0.071	6.38	3.99	4.46	2.48	1.25	4.6	106
M5 = (CN  " ,4CEPO2)	18	45.9	1.484	0.076	7.48	2.19	4.29	2.51	1.39	4.5	-
M4 = (ϕd_6CPS, 4CEPO2)	0	49.0	1.504	0.092	4.43	2.25	4.76	2.35	0.94	4.7	74
 4CEPO2	43	75.4	1.469	0.064	4.20	-0.91	5.93	3.14	1.05	5.9	120
	measured at: (T_c -10°C)										22°C

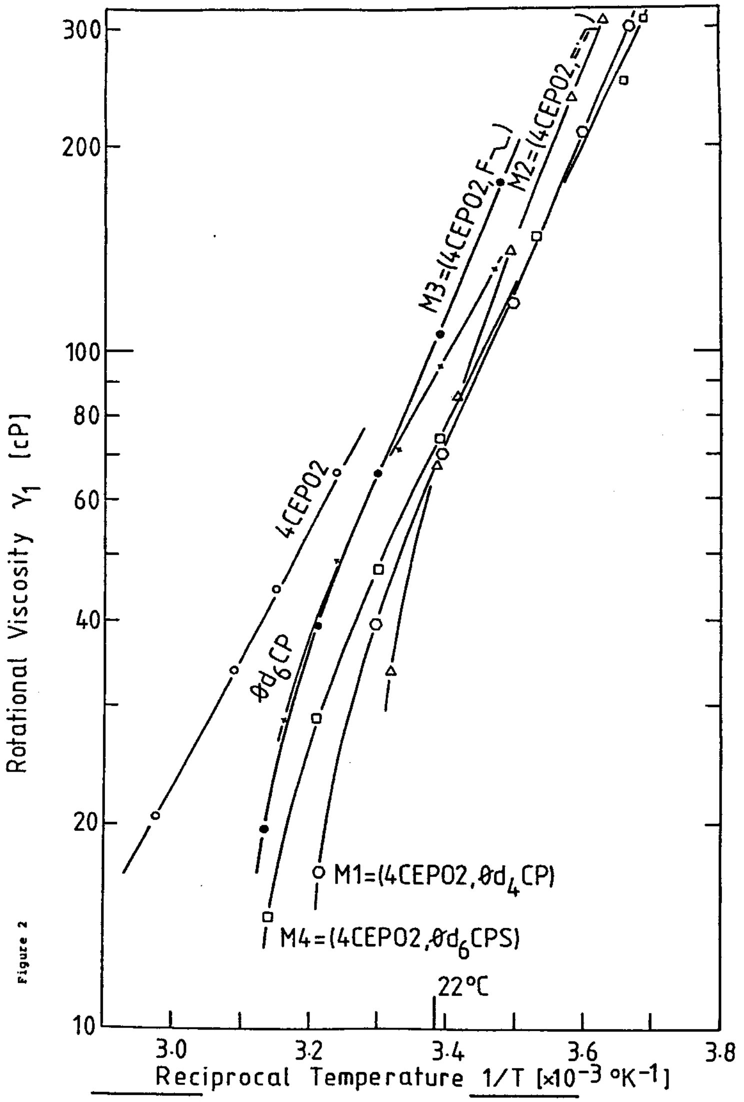


FIGURE 2 Temperature dependence of rotational viscosity γ_1 of the single components 4CEPO2 (c.f. structure at the bottom of Table V) and ϕd_6CP as well as of binary mixtures M1–M4 (Table V).

$\gamma_1(M1) \simeq \gamma_1(M4)$ despite the longer side-chain of ϕd_6CPS. This result confirms our earlier findings mentioned above and indicates that replacement of CN by NCS allows a simultaneous extension of the side-chain by C_2H_5 without increasing γ_1.

Despite the often strongly non-linear changes of elastic properties which occur when blending liquid crystal components belonging to different classes,[12] it seems that all terminal substituents in 4-position shown in Table V have low values of the twist elastic constants k_{22}. Therefore, and from the low values of $k_{22}(M1)$, $k_{22}(M4)$ (Table V) and $k_{22}(\phi d_6CPS)$ (Table IV) it appears that substitution at even side-chain positions favours low k_{22}-values. Moreover, from $\Delta\varepsilon(M5) >> 0$ in Table V it follows that the permanent cyano dipole moments of the cyano terminally substituted compound do not cancel each other, otherwise $\Delta\varepsilon$ would be near zero. This finding indicates that the angle between the terminal cyano group and the direction of the nematic director is rather large. This conclusion is supported by the large values of $\varepsilon_\perp$ (M5) in Table V and agrees with our earlier molecular modelling considerations which showed that the angle between the terminal double bond of ϕd_4CP and the long molecular axis of the molecule is non-zero.[1]

5. CONCLUSIONS

By a single step introduction of a terminally alkenylated side-chain into cyano and isothiocyanate phenylcyclohexanes, homologous series were synthesized consisting of new nematic mesogens with double bonds far removed from the rigid core. For compounds with odd alkenyl positions, broader mesomorphic temperature ranges were found than for their saturated counterparts; whereas even positions lead to narrower ranges. Terminal acetylene or allene groups were found to strongly depress the mesomorphic properties. Except for hydroxyl and aldehyde terminal groups, polar terminal substituents were also found to depress strongly the mesomorphic properties of liquid crystals.

From investigations into the dielectric, birefringence, viscous and all three elastic constants, we have found the alkenyl-position dependent odd–even effects depicted in Figure 3. This figure summarizes our findings on the position-dependent influence of the alkenyl double bond on k_{33}/k_{11}, $\kappa = k_{11} + (k_{33} - 2k_{22})/4$, Δn and $\Delta\varepsilon$. From the present investigations and our earlier findings[4] we conclude (i) that the dashed lines in Figure 3 indeed reflect the predicted per-

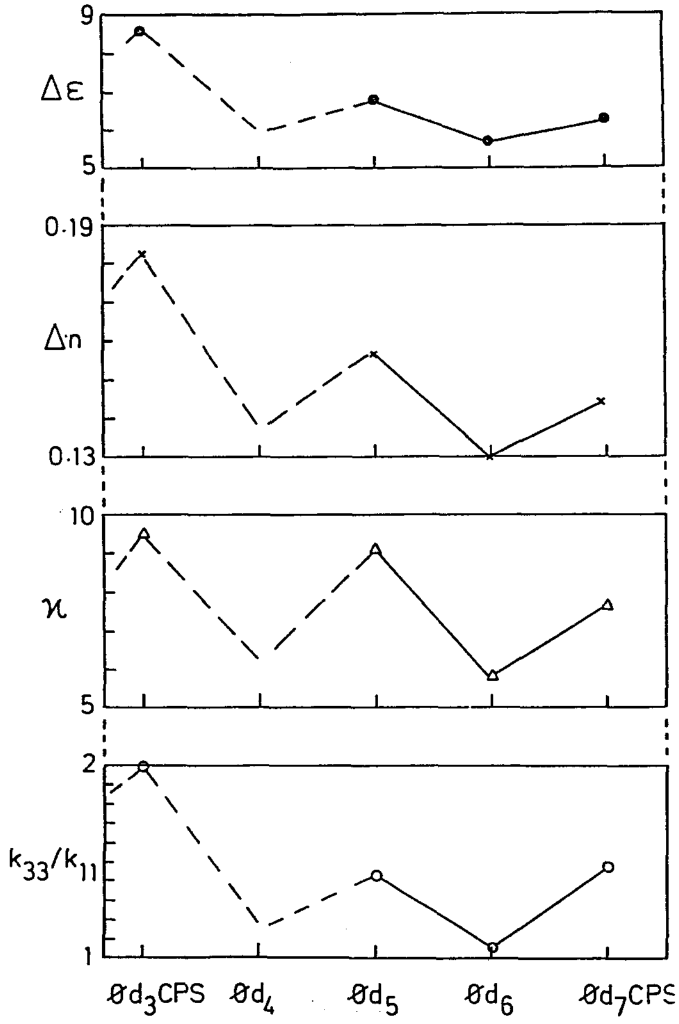


FIGURE 3 Summary of the alkenyl position-dependent odd-even effects found within the homologous series of $\phi d_i CPS$ ($i = 3, 4, 5, 6$ and 7) for k_{33}/k_{11}, κ, $\Delta\varepsilon$ and Δn. The dashed extrapolations are from references 1 and 4.

formance of the monotropic compound $\phi d_4 CPS$ and that (ii) an analogous odd–even behaviour occurs for the CN-alkenyls. Thus generalising from the above and our previous findings[1,4]: low values for k_{33}/k_{11}, κ, Δn and $\Delta\varepsilon$ occur for even alkenyl homologoues, that is, for $\phi d_{(2i)}CP$ and $\phi d_{(2i)}CPS$, with $i = 1, 2, 3, \ldots$; whereas the opposite holds for odd homologoues, i.e., $\phi d_{(2i+1)}CP$ and $\phi d_{(2i+1)}CPS$, with $i = 0, 1, 2, \ldots$ etc.

As far as we are aware, these findings are the first to show the position-dependence of induced dipole–dipole interaction (due to the alkenyl double bonds) in liquid crystals, and their consequence on elastic, dielectric and optical properties. The simultaneous occurrence of the odd–even effects depicted in Figure 3 shows that not only are Δn and $\delta\varepsilon$ related to each other *via* well known dielectric and sterical considerations,[1] but that the elastic properties of liquid crystals are also related (via induced dipole–dipole interactions) to their dielectric and/or optical properties. These findings agree with our earlier results which showed that the value of the ratio k_{33}/k_{11} increases with increasing dielectric anisotropy $\Delta\varepsilon$.[12]

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References

1. M. Schadt, M. Petrzilka, P. R. Gerber and A. Villiger, *Mol. Cryst. Liq. Cryst.*, **122**, 241–260 (1985).
2. M. Petrzilka, *Mol. Cryst. Liq. Cryst.*, **131**, 109 (1985).
3. M. Schadt and M. Petrzilka, *Proc. SID*, **26**, No. 2, 117–124 (1985).
4. M. Schadt, R. Buchecker, A. Villiger, F. Leenhouts and J. Fromm, Proc. 4th International Display Research Conference, San Diego, 231–234 (1985).
5. M. Schadt, R. Buchecker, F. Leenhouts, A. Boller, A. Villiger and M. Petrzilka, *Mol. Cryst. Liq. Cryst.* **139**, 1 (1986).
6. G. Fouquet and M. Schlosser, *Angew. Chem.*, **86**, 50 (1974).
7. D. E. Bergbreiter and G. M. Whitesides, *J. Org. Chem.*, **40**, 779 (1975).
8. R. Dabrowsky, J. Dziaduszek and T. Szczucinski, *Mol. Cryst. Liq. Cryst.*, **124**, 241 (1985).
9. G. F. Hennon and J. J. Sheehan, *J. Am. Chem. Soc.*, **71**, 1964 (1949).
10. M. Petrzilka, *Mol. Cryst. Liq. Cryst.*, **111**, 329, 347 (1984).
11. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, *Angew. Chem.*, **89**, 103 (1977).
12. M. Schadt and P. R. Gerber, *Z. Naturforsch.*, **37A**, 165 (1982).
13. D. Demus, H. J. Deutscher, F. Kerschel and H. Schubert, German Patent No. 2429093 (1973).