Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

New Liquid Crystals: The Synthesis and Mesomorphic Properties of Nematic Alkenylsubstituted Cyanophenylcyclohexanest

Martin Peterzilka [a]
[a] Central Research Units, F. Hoffmann-La Roche & Co., Ltd., CH-4002, Basle
Version of record first published: 20 Apr 2011.

To cite this article: Martin Peterzilka (1985): New Liquid Crystals: The Synthesis and Mesomorphic Properties of Nematic Alkenylsubstituted Cyanophenylcyclohexanest, Molecular Crystals and Liquid Crystals, 131:1-2, 109-123

To link to this article: http://dx.doi.org/10.1080/00268948508084197

Mol. Cryst. Liq. Cryst., 1985, Vol. 131, pp. 109–123
0026-8941/85/1312–0109/$20.00/0

Printed in the United States of America

New Liquid Crystals: The Synthesis and Mesomorphic Properties of Nematic Alkenylsubstituted Cyanophenylcyclohexanes†

MARTIN PETRZILKA

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

(*Received January 10, 1985*)

18 Alkenylsubstituted cyanophenylcyclohexanes have been synthesized by systematically varying both the position and the configuration of the isolated C,C-double bond. The influences of such structural changes on the mesomorphic properties‡ are discussed and the observed nematic thermal stabilities (cf. Table I) are compared with those of the corresponding fully saturated, alkyl analogs.

INTRODUCTION

During the past decade the synthesis of new nematic LC-materials has involved mainly the variation of either the central rigid core or the polar end group of such systems. As a consequence, little attention has been paid to the change of mesogenic properties resulting from structural modifications of apolar, terminal side chains such as alkyl groups. The most prominent alterations in this respect relate to the replacement of methylene groups, at various positions in the alkyl chain, by either oxygen[2] or difluoromethylene units.[3] In addition, by inserting acetylene units into the alkyl chains of typical nematogens we have recently found a new way of strongly influencing the transition temperatures of common LC-materials.[4] In this communication

†Presented in part at the 10th International Liquid Crystal Conference, York, England, July 15–21, 1984

‡For a presentation of other physical properties of these compounds cf. Ref. 1.

we present a further way of altering apolar side chains—the replacement of dimethylene groups by *E*- or *Z*-olefin units at various positions of the terminal alkyl chains in cyanophenylcyclohexanes has been investigated. The synthesis and mesomorphic properties of these new compounds will be discussed.

PREPARATION OF MATERIALS

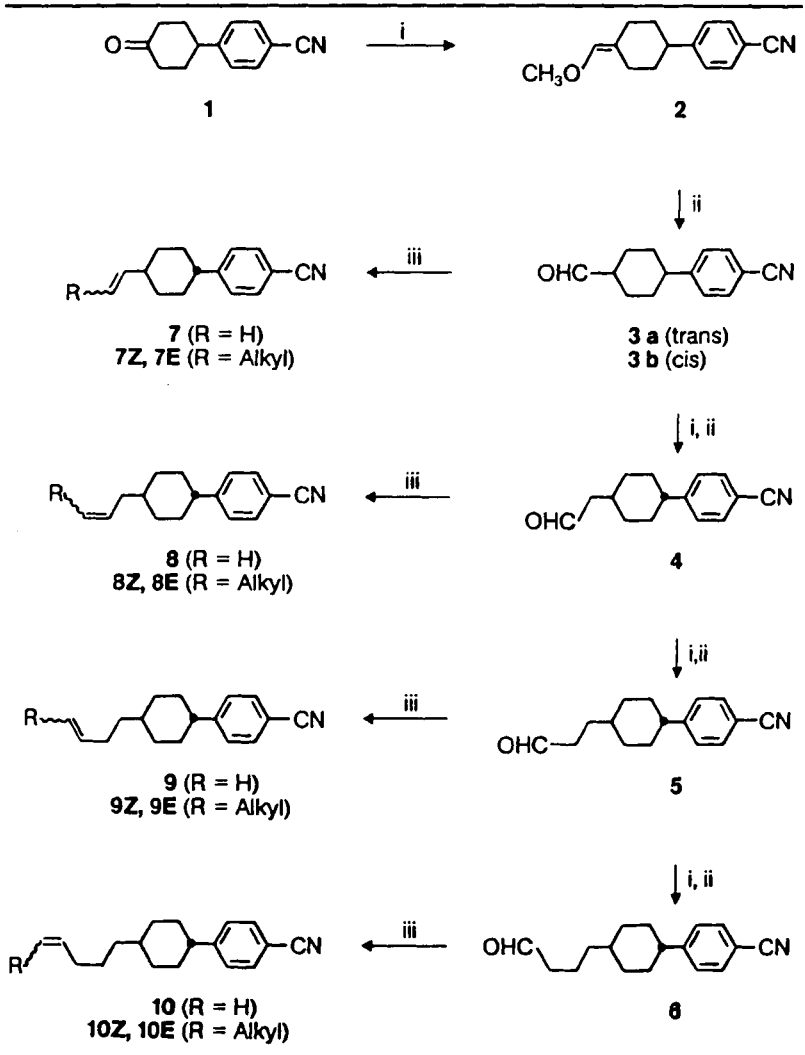
For a systematic study of the positional and constitutional influences of C,C-double bonds in terminal side chains on the transition temperatures, a large number of alkenylsubstituted cyanophenylcyclohexanes were needed. The synthetic strategies chosen for their preparation are summarized in Schemes 1 and 2, taking into account the problems involved with the generation of isolated *Z*- and especially *E*-olefins of high stereochemical purity in the presence of other functional groups.

Treatment of the known cyanoketone *1*[5] with the ylid derived from methoxymethyltriphenylphosphonium chloride, hydrolysis of the enolether *2* and subsequent crystallization of the resulting epimeric cyanoaldehyde mixture (*3a* : *3b* = 3 : 1) produced the *trans*-epimer *3a* in a stereochemically pure form. This bifunctional intermediate may be regarded as a common precursor to all of the desired final products, since these may be derived from *3a* by either single or repeated one carbon elongations of the aldehyde moiety in *3a* and/or introduction of the alkenyl side chains by the appropriate Wittig reactions (cf. Scheme 1).

Thus each of the four cyanoaldehydes *3a*, *4*, *5* and *6* allows for the appendage of vinyl- and *Z*- or *E*-alkenyl side chains as illustrated in Scheme 2 for the synthesis of cyano-olefins *7*, *7Z5* and *7E5*. Accordingly the reactions of *3a*, *4*, *5* and *6* with the ylid derived from methyltriphenylphosphonium bromide led directly to the pure vinyl-substituted nitriles *7*, *8*, *9* and *10*, whereas treatment of the same aldehydes with secondary Wittig salts in the presence of base produced *Z*/*E*-mixtures of cyano-olefins *7Z*/*7E*, *8Z*/*8E*, *9Z*/*9E* and *10Z*/*10E* consisting mainly of the corresponding *Z*-isomers. Depending on the position of the newly formed C,C-double bond, the *Z*/*E*-ratio varied from 77 : 23 up to 96 : 4 (cf. experimental part). If desired, the pure *Z*-isomers may then be obtained by additional chromatography on silica gel previously impregnated with silver nitrate.

Alternatively, for the preparation of the corresponding *E*-configurated nitriles *7E*, *8E* and *9E* the above mentioned *Z*/*E*-mixtures

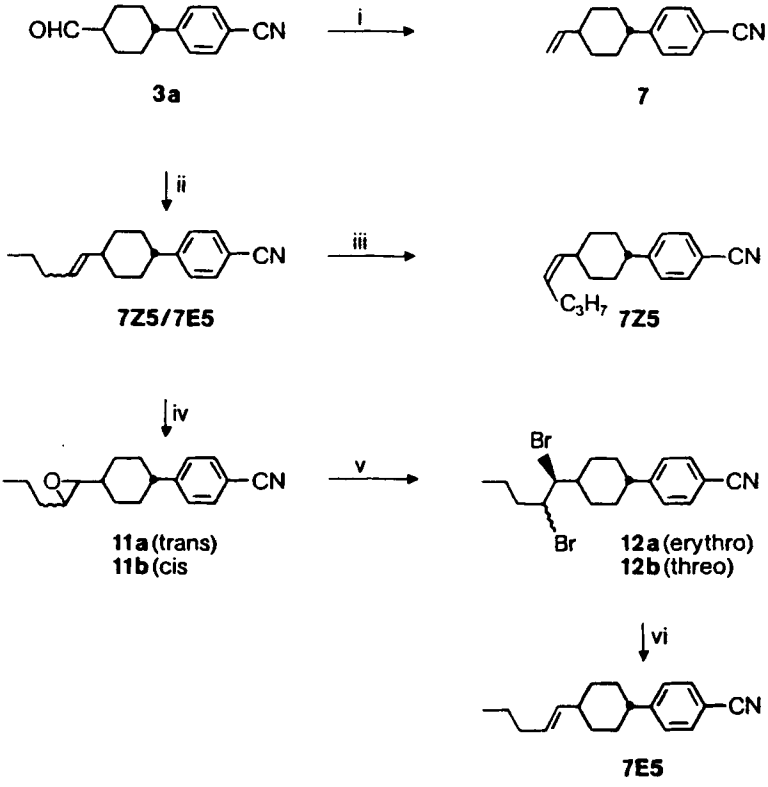
SCHEME 1[a]



i: $(C_6H_5)_3P^+CH_2OCH_3\ Cl^-$/t-BuOK; ii: THF-2N HCl 4:1; iii: *cf.* Scheme 2

[a] The letters *Z* and *E* refer to the geometry of the C,C-double bonds, *i.e.* Z = *cis* and E = *trans*. The number following these letters denotes the total number of carbon atoms in the alkenyl side chain.

SCHEME 2[a]



i: $(C_6H_5)_3P^+CH_3Br^-$/n-BuLi; ii: $(C_6H_5)_3P^+(CH_2)_3CH_3\ Br^-$/t-BuOK; iii: chromatography on $SiO_2.AgNO_3$; iv: MCPBA/K_2CO_3; v: $(C_6H_5)_3P.Br_2$; vi: Zn/AcOH

[a] For the abbreviations used *cf.* footnote a in Scheme 1.

were subjected to a three-step olefin-inversion procedure (cf. Scheme 2) originally developed by Sonnet.[6] By this operation, mixtures of cyano-olefins resulted which showed an approximately inverted *Z*/*E*-ratio, i.e. were rich in *E*-isomers. For the isolation of pure *trans*-1-alkenylsubstituted nitriles *7E* it was found advantageous to purify at the stage of the intermediate *erythro*-dibromides (e.g. *12a*), since these, by virtue of their crystalline character, could be crystallized easily, and in addition, were transformed stereospecifically to the desired nitriles *7E* by treatment with zinc in acetic acid. On the other hand, the purification of *trans*-2- and *trans*-3-alkenylsubstituted ni-

triles *8E* and *9E*, respectively, was accomplished by either chromatography on silver nitrate impregnated silica gel or crystallization of the corresponding inverted *Z/E*-mixtures of cyano-olefins *8Z/8E* and *9Z/9E*.

Finally it is worth mentioning that the Wittig reactions leading to 1-alkenylsubstituted nitriles *7* and *7Z/7E* or to the homologous cyanoaldehyde *4* have to be carried out at generally lower temperatures (cf. experimental part) in order to preserve the previously established *trans*-stereochemistry of the cyclohexane moiety in aldehyde *3a*.

RESULTS AND DISCUSSION

The mesomorphic properties of the new alkenylsubstituted cyanophenylcyclohexanes are summarized in Table 1. By comparing these data with each other or with those of the corresponding hydrogenated counterparts, a number of conclusions may be drawn which allow for the estimation of the positional and configurational influence of C,C-double bonds in alkenyl side chains on the transition temperatures. In the following, some examples of such comparisons are presented.

The influence of the position of C,C-double bonds

In principle, the isolated olefin units of alkenylsubstituted cyanophenylcyclohexanes may be located at different positions with regard to the cyclohexane ring. The influence of shifting such a double bond on the transition temperatures is demonstrated in Figures 1 and 2 by either varying or keeping constant the total length of the terminal alkenyl chains.

By inspection of these curves the following conclusions can be drawn:

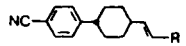
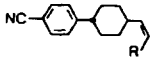
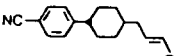
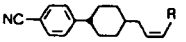
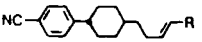
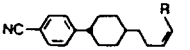
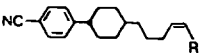
In both series of compounds a very strong alternation of the T_c-values is observed (Figures 1 and 2).

In the case of 1-alkenylsubstituted cyanophenylcyclohexanes (Figure 1) this alternation of the clearing points (T_c) is (i) much more pronounced than that of the correspondingly hydrogenated counterparts and (ii) *opposite* to the usually observed one, i.e. members with an even number of carbon atoms in the side chain exhibit high T_c-values whereas odd-membered representatives show low T_c-values.

In both series the melting points (T_m) are generally less affected

TABLE 1[a]

Transition temperatures and enthalpies of alkenylsubstituted cyanophenylcyclohexanes.

Abbreviation[b]	Compound	R	T_m (°C)	T_c (°C)	T_c-T_m (°C)	ΔH (kcal/mol^{-1})
7		H	56.4	(28.5)	-27.9	4.15
7E3		CH_3	66.3	73.0	6.7	4.76
7E4		C_2H_5	45.1	51.8	6.7	3.60
7E5		C_3H_7	15.6	58.5	42.9	2.54
7E6		C_4H_9	14.4	39.2	24.8	4.40
7E7		C_5H_{11}	17.9	49.2	31.3	4.39
7Z5		C_3H_7	—	[-144]	—	—
8		H	29.2	[-30.5]	-59.7	5.11
8E5		C_2H_5	16.1	[-67.0]	-83.1	—
8Z5		C_2H_5	-7.7	[-54.0]	-61.7	—
9		H	49.5	52.5	3.0	3.63
9E5		CH_3	59.8	73.7	13.9	4.57
9E6		C_2H_5	31.1	50.2	19.1	3.06
9E7		C_3H_7	15.4	48.3	32.9	4.59
9Z5		CH_3	33.1	(-13.7)	-46.8	5.09
10		H	29.8	(10.2)	-19.6	5.29
10Z6		CH_3	27.4	(4.5)	-22.9	6.25

[a] Abbreviations used in Tables 1–2 and Figures 1–3:

$T_m = T_{K-N}$ = melting point (°C)

$T_c = T_{N-I}$ = clearing point (°C), a monotropic transition temperature is denoted by ( ) brackets around the recorded temperature, whilst a virtual value is signified by a [ ] bracket; the latter were determined in ROTN-653 (T_c = 72,8°C)). None of the compounds listed exhibited any smectic phases.

T_c-T_m = meso-range, a negative sign indicates monotropy.

ΔT_c = Difference in clearing points of two compounds; a positive sign denotes a higher clearing point for the compound listed on top and vice versa.

E/*Z* = Indicates the geometry of the olefinic unit (*E* = *trans*, *Z* = *cis*.

[b] For an explanation of these abbreviations *cf.* footnote a in Scheme 1.

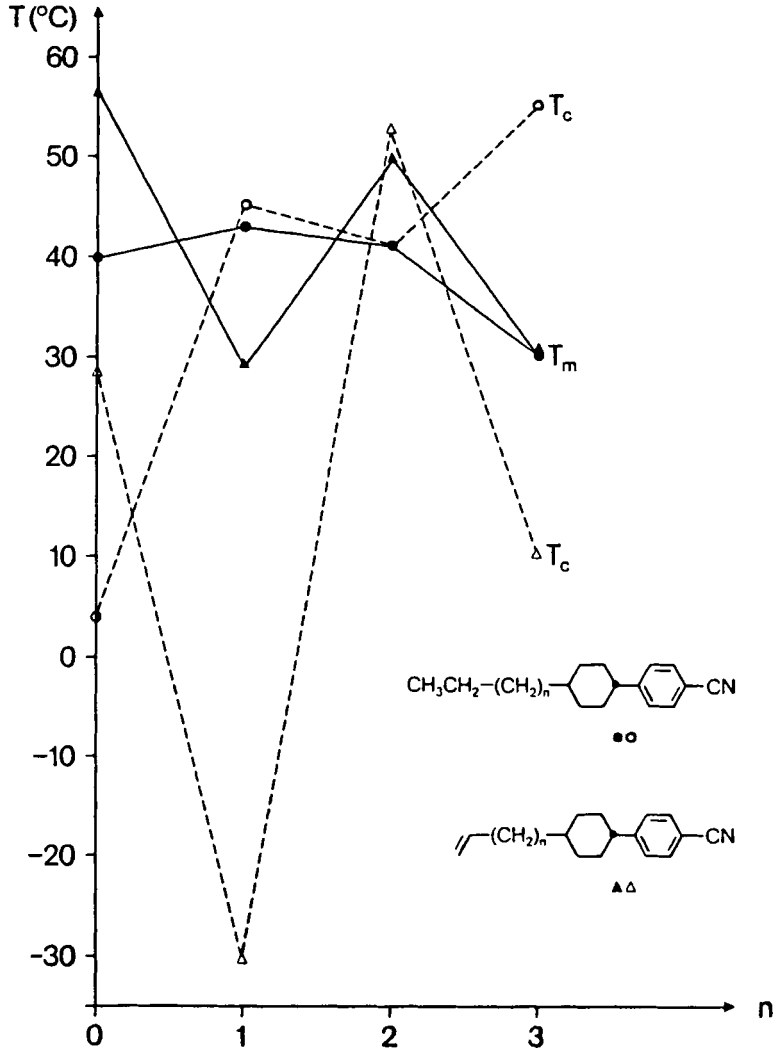


FIGURE 1 Transition temperatures of homologous series of alkyl- and ω-alkenyl-substituted cyanophenylcyclohexanes

and alternate on parallel lines to the T_c-values albeit less markedly (Figures 1 and 2).

In addition, by comparing 1-alkenyl- with 3-alkenylsubstituted cyanophenylcyclohexanes (cf. Figure 3), it can be shown that shifting an *E*-olefin unit from the 1- (*7E*) to the 3-position (*9E*) in general causes a rise in both T_m and T_c.

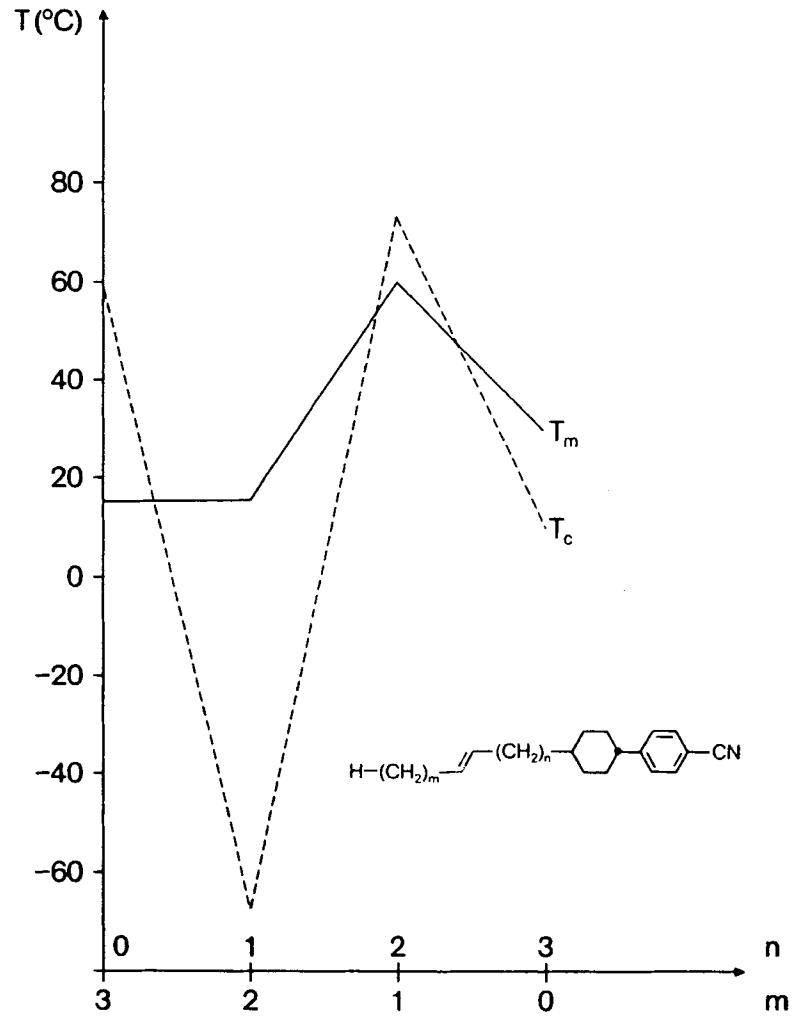


FIGURE 2 Transition temperatures of isomeric E-pentenylsubstituted cyanophenylcyclohexanes

In summary, the position of an isolated C,C-double bond exerts a moderate influence on the melting points and a crucial influence on the clearing points of alkenylsubstituted cyanophenylcyclohexanes.

Alkyl- versus 1- or 3-alkenyl side chains

In Figure 3 the transition temperatures of two homologous series of 1- and 3-*E*-alkenylsubstituted cyanophenylcyclohexanes are plotted against the number (n) of carbon atoms of their side chains.

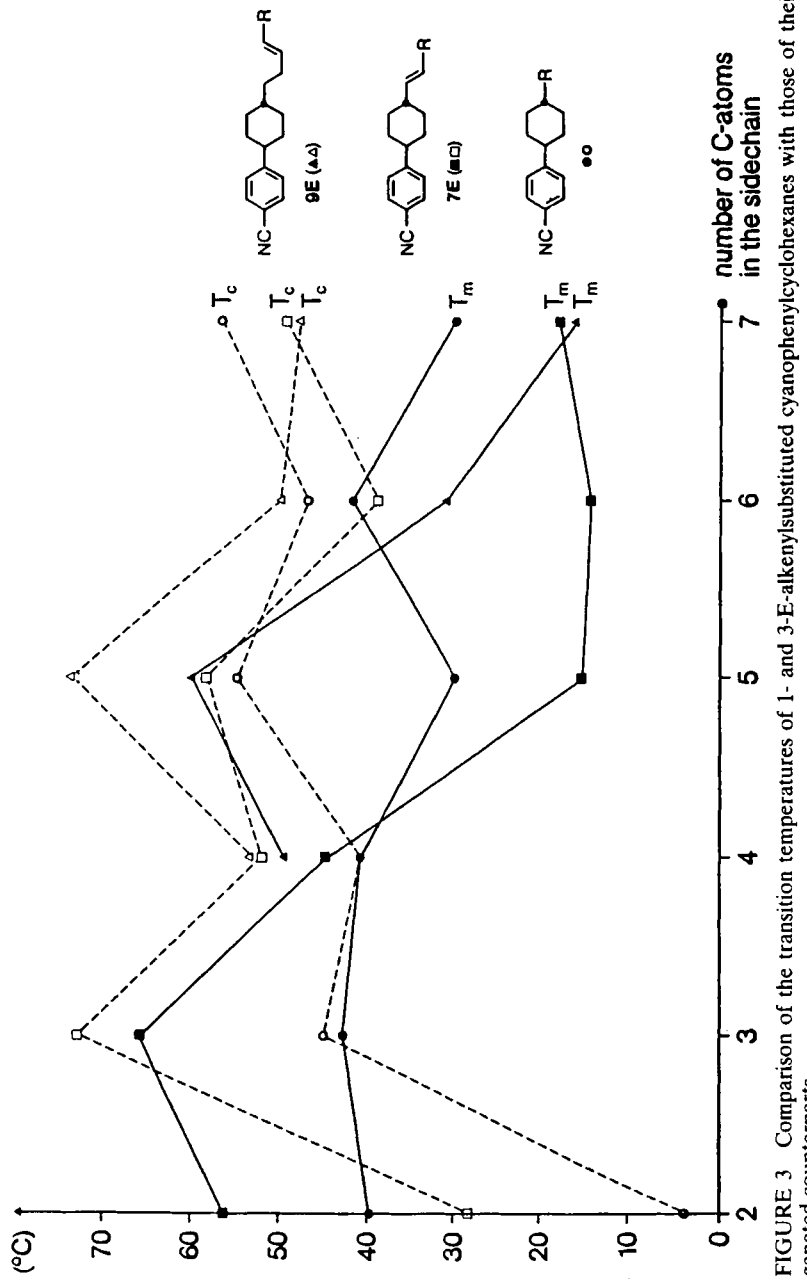


FIGURE 3 Comparison of the transition temperatures of 1- and 3-E-alkenylsubstituted cyanophenylcyclohexanes with those of their hydrogenated counterparts

By comparing these values with those of the corresponding hydrogenated counterparts the following tendencies can be observed:

Short-membered representatives of the nitriles *7E* (n = 2,3) show higher melting points (T_m), whereas those with longer side chains (n = 5,7 and especially 6) attract notice by their considerably lower T_m-values.

With the exception of nitriles *7E* (n = 6,7) and nitrile *9E* (n = 7) all other homologues in these two series exhibit higher clearing points (T_c).

The mesoranges (T_c-T_m) are generally broader for the new nitriles *7E* and *9E*; for an exception cf. nitrile *9E* (n = 5).

Thus with regard to the mesomorphic properties the new cyanoolefins *7E* and *9E* compare well with the corresponding alkylsubstituted analogs.

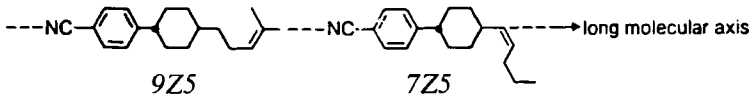
The influence of the configuration of C,C-double bonds

Due to the possible existence of 1,2-disubstituted olefins as geometrical isomers (*E* or *Z*), the influence of the configuration of C,C-double bonds in alkenylsubstituted cyanophenylcyclohexanes on the transition temperatures may be studied additionally. For this purpose the mesomorphic properties of three E/Z pairs, which differ only by the location of the corresponding olefin units, are compared with each other in Table 2.

The following comments appear to be valuable:

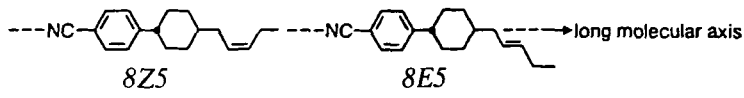
Depending on the position of the olefin unit, either the *E*-isomer (e.g. *7E5* and *9E5*) or the *Z*-isomer (e.g. *8Z5*) of a corresponding *E*/*Z*-pair induces a higher clearing point (T_c).

The considerably higher T_c-value of *9Z5*, as compared to that of *7Z5*, may be ascribed to a better alignment of the alkenyl side chain along the molecular axis.



9Z5 *7Z5*

A similar argument may be used to explain the fact that *8Z5* induces lower depressions of T_c in mixtures than the isomeric *8E5*. In the latter case, the optimal U-shape of the side chain cannot be further adopted.



8Z5 *8E5*

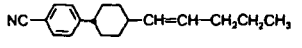
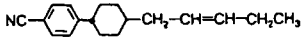
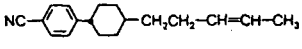
Accordingly, the configuration of 1,2-disubstituted C,C-double bonds appears to play an equally important role in determining the height of the clearing points of alkenylsubstituted cyanophenylcyclohexanes. This *E/Z*-effect is position-dependent and is most pronounced if the olefinic unit is located next to the cyclohexane ring (ΔT_c = 202,5°C).

CONCLUSIONS

By replacement of a dimethylene unit by a C,C-double bond at different positions in the alkyl side chains of cyanophenylcyclohexanes, a new mode of altering terminal side chains is presented. The influence of such structural changes on the mesomorphic properties is strongly dependent on both the position and configuration of the inserted C,C-double bonds. Accordingly, some of the new olefinic nitriles exhibit higher T_c-values and/or broader mesoranges (T_c-T_m)

TABLE 2[a]

Comparison of the transition temperatures of *E/Z*-isomeric pairs of alkenylsubstituted cyanophenylcyclohexanes.

Abbreviation	Compound	E/Z	T_m (°C)	T_c (°C)	T_c-T_c (°C)	ΔT_c (°C)
7E5		E	15.6	58.5	42.9	202.5
7Z5		Z	—[b]	[-144]	—	
8E5		E	16.1	[-67]	-83.1	-13.0
8Z5		Z	-7.7	[-54]	-61.7	
9E5		E	59.8	73.7	13.9	87.4
9Z5		Z	33.1	(-13.7)	-46.8	

[a] For the abbreviations used *cf.* footnotes a and b in Table 1.
[b] Oily compound, which could not be crystallized.

if compared with the corresponding alkylsubstituted analogs, whereas others behave in the opposite direction.

Acknowledgments

I wish to thank Mr. J. Reichardt and Miss S. Schmiederer for their competent collaboration during the preparation of the new materials and Mr. F. Wild and B. Halm for carrying out the differential thermal analyses.

EXPERIMENTAL

General

All reactions were carried out under argon. Solvents were passed through alumina (activity I) or distilled before use. Usual workup refers to successive washing of the organic phases with sat.aq. $NaHCO_3$-solution and/or H_2O and sat.aq. NaCl-solution followed by drying ($MgSO_4$ or K_2CO_3) and removal of the solvents at reduced pressure. Thin layer chromatography (TLC) was performed using Merck 0.25 mm (60 F 254) silica gel plates. Preparative flash chromatography was carried out according to Still[7] at a pressure of 0.5 bar using silica gel (Merck, 230–400 mesh). The transition temperatures and enthalpies of the new compounds, listed in Table 1, were determined on a Mettler DTA TA 2000 and are corrected. Gas chromatography (VPC) was carried out on a Perkin-Elmer Sigma 3B + 10B using a glass column (2.2 mm ID, 2.0 m, stationary phase Gaschrom Q 120/140 mesh coated with 2% *trans*-4-(p-propylphenyl)-cyclohexyl-4′-(*trans*-4-pentylcyclohexyl)-4-biphenylcarboxylate) at 6.5 bar N_2 and temperatures of 170–220° (isotherm). All IR, ^{1}H-NMR and mass spectra of the new compounds are in agreement with their assigned structures.

Preparation of cyanoaldehydes 3a, 4, 5 and 6

To a slurry of 10.4 g (30.3 mmol) of (methoxymethyl)-triphenylphosphonium chloride in 60 ml of dry t-butyl methyl ether at −10°C, 3.6 g (32.1 mmol) of solid t-BuOK was added over 10 min. After stirring an additional 30 min at 0°C, a solution of 4.2 g (21.1 mmol) of *1*[5] in 50 ml of dry THF was added over 5 min to the deep-orange mixture. Stirring was continued for 2 h at RT before the reaction mixture was poured into 500 ml of hexane and filtered through a pad of Celite. Flash chromatography of the concentrated filtrate on silica gel (ethyl acetate/petroleum ether 1 : 19) produced

4.5 g (94%) of enolether *2* as a colourless, slowly crystallizing oil (purity according to VPC: 95%).

14.3 g (62.7 mmol) of likewise obtained *2* was dissolved in 200 ml of 2N HCl/THF 1:4 and heated to reflux for 30 min. Dilution with water (300 ml) and extraction with ether (3 × 200 ml) followed by the usual workup gave 13.7 g of a colourless semicrystalline mass, consisting (NMR, VPC) of an epimeric mixture of cyanoaldehydes *3a* : *3b* = 3:1. Crystallization of this material from 1.3 l of hexane (55°C → RT) furnished 3.7 g (29%) of *3a* as long colourless needles, m.p. 57.1°C (purity according to VPC: 99.5%).

By repeating once, twice or thrice the above procedure, *3a* was converted to the homologous cyanoaldehydes *4*, *5* and *6*, respectively, in yields of 70–90%. Unlike the oily *5* and *6* cyanoaldehyde, *4* could be crystallized from hexane/t-butyl methyl ether, m.p. 43.4°C.

Preparation of ω-alkenylsubstituted nitriles *7*, *8*, *9* and *10*

To a slurry of 2.51 g (7.0 mmol) of methyltriphenylphosphonium bromide in 80 ml of dry THF at −20°C, 7.6 ml of a 0.8 M solution of n-butyllithium in hexane was added over 5 min. After stirring an additional 30 min at −20°C, a solution of 1.0 g (4.7 mmol) of *3a* in 10 ml of dry THF was added over 5 min to the yellow mixture. Stirring was continued for 30 min at −20°C before the reaction mixture was poured into 100 ml of water. Extraction with ether (3 × 100 ml), followed by the usual workup, furnished a crystalline residue, which upon flash chromatography on silica gel (ethyl acetate/petroleum ether 3 : 97), produced 897 mg (91%) of nitrile *7* as colourless crystals (purity according to VPC: 99.4%). By additional crystallization from methanol (50°C → −20°C), analytically pure *7* was obtained. TLC (ethyl acetate/petroleum ether 3 : 97): R_f (*7*) 0.13.

Following the above procedure the aldehydes *4*, *5* and *6* were converted to the nitriles *8*, *9* and *10*, respectively, in yields of 72–80%.

Preparation of the Z-configurated cyano-olefins *7Z5*, *8Z5*, *9Z5* and *10Z6*

To a slurry of 3.6 g (9.0 mmol) of butyltriphenylphosphonium bromide in 40 ml of t-butyl methyl ether at RT, 1.0 g (9.0 mmol) of solid t-BuOK was added at once. After stirring an additional hour at RT, a solution of 1.28 g (6.0 mmol) of aldehyde *3a* in 10 ml of t-butyl methyl ether was added over 15 min to the cooled (−60°) deep-orange mixture. Stirring was continued for 1h at −30°C before the

reaction mixture was poured into 100 ml of water. Extraction with ether (3 × 50 ml), followed by the usual work up, furnished an oily residue, which upon flash chromatography on silica gel (ethyl acetate/ petroleum ether 3 : 97) gave 1.52 g (99%) of a colourless oil. According to VPC-analysis, this material consisted of a mixture of cyano-olefins *7Z5* : *7E5* = 95:5, from which the pure Z-isomer *7Z5* could be obtained by chromatography on silica gel (pretreated with a 0.2 M solution of silver nitrate in acetonitrile and dried) using ethyl acetate/petroleum ether 3 : 97 as the eluting solvent system. TLC (SiO_2 impregnated with $AgNO_3$, ethyl acetate/ petroleum ether 3 : 97): R_f (*7E5*) 0.23, R_f (*7Z5*) 0.14.

Following the above procedure, aldehyde *3a* was converted to *7Z3* : *7E3* = 95 : 5, *7Z4* : *7E4* = 96 : 4, *7Z6* : *7E6* = 95 : 5 and *7Z7* : *7E7* = 95 : 5, aldehyde *4* to *8Z5* : *8E5* = 92 : 8, aldehyde *5* to *9Z5* : *9E5* = 86 : 14, *9Z6* : *9E6* = 91 : 9 and *9Z7* : *9E7* = 93 : 7 and aldehyde *6* to *10Z6* : *10E6* = 77 : 23 in comparable yields. The pure Z-isomers *8Z5*, *9Z5* and *10Z6* were then obtained by analogous chromatography of the corresponding *E*/*Z*-mixtures on silica gel impregnated with silver nitrate (see above).

Preparation of the E-configurated cyano-olefins *7E5*, *7E3*, *7E4*, *7E6*, *7E7*, *8E5*, *9E5*, *9E6* and *9E7*

To a mixture of 1.51 g (7.9 mmol) of m-chloroperbenzoic acid and 3.0 g (21.7 mmol) of powdered potassium carbonate in 60 ml of dry methylenechloride at 0°C, a solution of 2.0 g (7.9 mmol) of a mixture of cyano-olefins *7Z5* : *7E5* = 95 : 5 (*cf.* preceding experiment) in 20 ml of dry methylenechloride was added over 15 min. After stirring an additional 75 min by allowing the mixture to slowly warm up to RT, another 1.51 g (7.9 mmol) of m-chloroperbenzoic acid was added. Then the heterogeneous reaction mixture was stirred for another 3h at RT before it was poured into 50 ml of 10% sodium thiosulfate solution. Extraction with methylenechloride (3 × 100 ml), followed by washing the organic layers with sat. sodiumcarbonate solution, and the usual work up, furnished 2.1 g (98%) of a mixture of epoxides *11a* : *11b* = 5 : 95 as a colourless oil. TLC (ethyl acetate/petroleum ether 1 : 9): R_f (*11a*) 0.17, R_f (*11b*) 0.14.

To a solution of 2.46 g (9.4 mmol) of triphenylphosphine in 30 ml of dry methylenechloride at 0°C, a *ca.* 1 M solution of bromine in methylene chloride was added dropwise until a slight yellow colour persisted. The solvent was carefully (foaming) removed at reduced pressure and the solid residue suspended in 30 ml of dry benzene. To this was added a solution of the above obtained 2.1 g (7.80 mmol)

of epoxides *11a/11b* in 10 ml of dry benzene and the reaction mixture was heated to reflux for 3h. Subsequently the lukewarm reaction solution was filtered through a short column of silicagel (toluene) and the eluate evaporated to dryness. Flash chromatography of the crystalline residue on silica gel (hexane/toluene 1 : 1) furnished 2.61 g (81%) of *erythro*-dibromide *12a*, which after additional crystallization from ethyl acetate/petroleum ether 1 : 2 (55°C → 0°C), produced 2.09 g (65%) of analytically pure *12a* as colourless crystals, m.p.: 140.9°C. TLC (ethyl acetate/petroleum ether 1 : 9): R_f (*12a*) 0.41, R_f (*12b*) 0.25.

To a solution of 2.35 g (5.7 mmol) of likewise obtained *erythro*-dibromide *12a* in 20 ml of glacial acetic acid at RT, 2.42 g (37.0 mmol) of zinc dust was added at once (slightly exothermic). After stirring for an additional 2h, the reaction mixture was poured into 100 ml of water. Extraction with petroleum ether (3 × 100 ml), followed by the usual work up, furnished 1.43 g (99%) of nitrile *7E5* as a liquid crystalline compound (purity according to VPC: 99.5%). TLC (ethyl acetate/petroleum ether 1 : 9): R_f (*7E5*) 0.53.

Following the above procedures the cyano-olefins *7E3*, *7E4*, *7E6*, *7E7*, *8E5*, *9E5*, *9E6* and *9E7* were obtained in comparable yields. However, owing to the low crystalline character of the dibromides corresponding to the nitriles *8E5*, *9E5*, *9E6* and *9E7*, no purification by crystallization at this stage was possible. The crude mixtures of dibromides were therefore carried through the following zinc reduction and the resulting Z/E-mixtures of cyano-olefins (rich in E-isomers) were purified by either chromatography on silica gel impregnated with silver nitrate (*8E5*), crystallization from methanol (*9E5*) or by both techniques of purification (*9E6*, *9E7*).

References

1. M. Schadt, M. Petrzilka, P. R. Gerber and A. Villiger, *Mol. Cryst. Liq. Cryst.*, submitted for publication.
2. T. Kitamura, A. Mukoh and T. Fujii, *Mol. Cryst. Liq. Cryst.*, **108**, 333 (1984); H. Inoue, T. Inukai, Y. Goto, H. Sato, M. Fukui and K. Yokohama, German Patent Application DE 3237020 (1982); Y. Hirai, T. Fujii, K. Koto, K. Suzuki, M. Yoshida, H. Okawa, T. Kitamura, H. Yokokura, Y. Okabe, S. Hattori, A. Mukoh and M. Sato, European Patent Application 0058981 (1982).
3. R. Eidenschink, D. Erdmann, J. Krause and L. Pohl, German Patent Application DE 2927277 (1979).
4. M. Petrzilka, *Mol. Cryst. Liq. Cryst.*, **111**, 329 (1984).
5. M. Osman and L. Révész, *Mol. Cryst. Liq. Cryst.*, **56**, 133 (1980).
6. P. E. Sonnet, *Tetrahedron*, **36**, 557 (1980) and references cited therein.
7. W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).