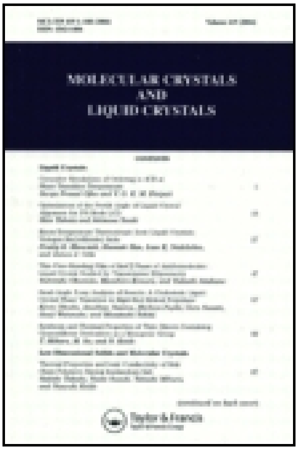

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New Liquid Crystals: The Synthesis and Mesomorphic Properties of Alkenylsubstituted Cyanophenylethylcyclohexanes and Cyanobiphenylylcyclohexanes

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New Liquid Crystals: The Synthesis and Mesomorphic Properties of Alkenylsubstituted Cyanophenylethylcyclohexanes and Cyanobiphenylylcyclohexanes†

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Nineteen alkenylsubstituted cyanophenylethylcyclohexanes and cyanobiphenylylcyclohexanes 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, where possible, with those of the corresponding saturated alkyl analogs.

INTRODUCTION

Recently we have reported on an attractive mode of altering the apolar side chains of cyanophenylcyclohexanes.[1] Accordingly it was discovered that the replacement of dimethylene elements by *E*- or *Z*-olefin units at various positions of the terminal alkyl groups in cyanophenylcyclohexanes strongly influences the transition temperatures of these nematics. In the light of these findings the question arose, whether analogous structural changes in other well known classes of LC-materials would affect the mesomorphic properties in a

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similar way, thus rendering this new structure-property relationship a more general validity.

Therefore, in this communication the influences of such structural modifications in cyanophenylethylcyclohexanes and cyanobiphenylylcyclohexanes have been investigated. In the following, the synthesis and mesomorphic properties of these new compounds will be discussed.

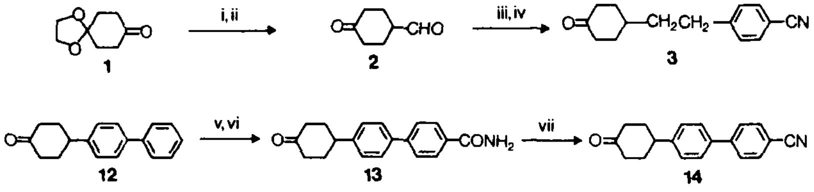
PREPARATION OF MATERIALS

The synthetic strategies chosen for the preparation of the new compounds are summarized in Schemes 1, 2 and 3 and parallel essentially those applied previously to the synthesis of the corresponding cyanophenylcyclohexanes.[1] The key intermediates required for such an approach are the bifunctional cyanoketones *3* and *14*, whose preparations are delineated in Scheme 1.

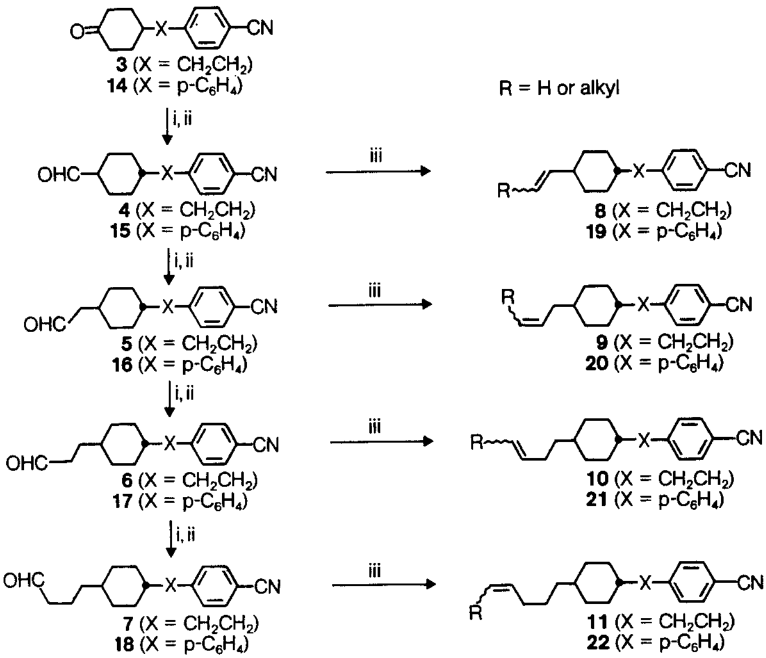
Thus selective Wittig-reaction of the ketoaldehyde *2*, resulting from C-1 homologation of the known ethylenedioxycyclohexanone *1*,[2] with the ylid derived from p-cyanobenzyltriphenylphosphonium chloride followed by catalytic hydrogenation of the newly generated C,C-double bond produced *3* in good yield.

On the other hand Friedel-Crafts acylation of 4-biphenylylcyclohexanone *12*[3] with oxalyl chloride and subsequent transformation of the resulting acid chloride moiety to a nitrile function offered an efficient preparation of the tricyclic cyanoketone *14*.

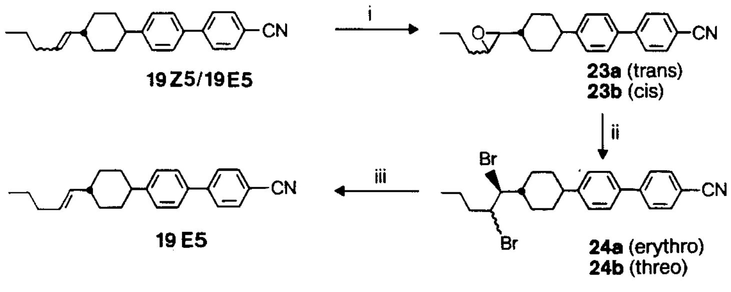
Single or repeated one carbon elongations of the ketone moieties in *3* or *14* *via* Wittig-reaction with the ylid derived from methoxymethyltriphenylphosphonium chloride, hydrolysis and subsequent crystallization then led to the cyanoaldehydes *4*, *5*, *6*, *7*, *15*, *16*, *17* and *18*, respectively. These in turn allowed for the appendage of vinyl- and *Z*- or *E*-alkenyl side chains as illustrated in Schemes 2 and 3. Accordingly the reactions of *4*, *5*, *6*, *7*, *15*, *16*, *17* and *18* with the



Scheme 1
i: $(C_6H_5)_3P^+CH_2OCH_3$ Cl^-/t-BuOK; ii:THF-2N HCl 4:1; iii: p-$CNC_6H_4CH_2P^+(C_6H_5)_3$ Cl^-/t-BuOK; iv: H_2/5% Pd-C; v: $(COCl)_2/AlCl_3$; vi: NH_4OH; vii: $C_6H_5SO_2Cl$/Pyr.



Scheme 2
i: $(C_6H_5)_3P^+CH_2OCH_3$ Cl^-/t-BuOK; ii: THF-2N HCl 4:1; iii: $(C_6H_5)_3P^+CH_2R$ Br^-/ t-BuOK



Scheme 3[a]
i:MCPBA/K_2CO_3; ii: $(C_6H_5)_3P.Br_2$; iii: Zn/AcOH
[a]For an explanation of the numbering system used cf. footnote a in table I.

ylid derived from methyltriphenylphosphonium bromide led directly to the pure vinylsubstituted nitriles *8*, *9*, *10*, *11*, *19*, *20*, *21* and *22*(R = H), respectively, whereas treatment of the aldehydes *4*, *6*, *15*, *16* and *17* with secondary Wittig salts in the presence of base produced *Z*/*E*-mixtures of cyano-olefins *8Z*/*8E*, *10Z*/*10E*, *19Z*/*19E*, *20Z*/*20E* and *21Z*/*21E* (R = alkyl) consisting mainly of the corresponding *Z*-isomers. Depending on the position of the newly formed C,C-double bond and the total chain length, the *Z*/*E*-ratio varied from 88:12 up to 97:3 (*cf.* experimental part). In one case (*20Z5*) the pure *Z*-isomer was then obtained by additional crystallization of the primary Wittig product.

For the preparation of the *E* nitriles *8E*, *10E*, *19E*, *20E* and *21E* the above mentioned *Z*/*E*-mixtures were subjected to Sonnet's[4] three-step olefin inversion procedure as demonstrated for *19E5* in Scheme 3. From 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 the pure *E*-alkenylsubstituted nitriles it was found advantageous to purify at the stage of the intermediate *erythro*-dibromides (e.g. *24a*), since these, by virtue of their crystalline character, could be crystallized easily, and in addition, were transformed stereospecifically to the desired *E*-configurated olefins by reductive debromination with zinc in acetic acid.

RESULTS AND DISCUSSION

The mesomorphic properties of the new alkenylsubstituted cyanophenylethylcyclohexanes and cyanobiphenylylcyclohexanes are summarized in Table I. By comparing these data with each other or with those of the corresponding hydrogenated counterparts, a number of conclusions may be drawn. In the following, some examples of such comparisons are presented, which demonstrate the influence of the position and configuration of inserted, isolated C,C-double bonds on the transition temperatures.

Cyanophenylethylcyclohexanes

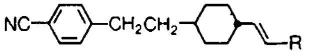
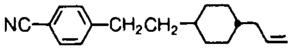
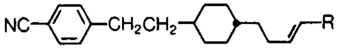
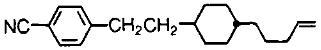
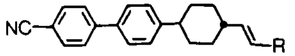
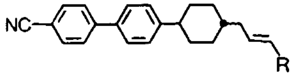
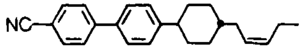
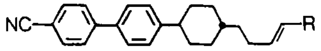
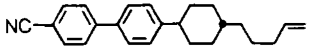
In Figure 1 the transition temperatures of a homologous series of 1-*E*-alkenylsubstituted cyanophenylethylcyclohexanes are plotted against the lengths of the terminal side chains.

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

—Short-membered representatives (*n* = 0,1,2) exhibit both higher T_m- and T_c-values, whereas those with longer side chains (*n* = 3,4,5) behave in the opposite way, i.e. they have lower melting and clearing points.

TABLE I

Transition temperatures and enthalpies of alkenylsubstituted cyanophenylethylcyclohexanes and cyanobiphenylylcyclohexanes

Code[a]	Compound	R	T_{C-N}[b] (°C)	T_{N-I}[c] (°C)	ΔT[d] (°C)	ΔH (kcal/mol)
8		H	55.8	[15][e]	−40.8	6.41
8E3		CH_3	61.3	(54.2)	−7.1	6.12
8E4		C_2H_5	42.6	(39.7)	−2.9	4.07
8E5		C_3H_7	25.1	47.5	22.4	3.63
8E6		C_4H_9	19.7[f]	34.6	18.2	5.10
8E7		C_5H_{11}	31.6	43.6	12.0	5.24
9			39.7	(−9.3)	−49.0	5.83
10		H	41.0	47.5	6.5	4.23
10E5		CH_3	44.0	65.6	21.6	
11			25.3	(17.2)	−8.1	7.03
19		H	150.4	234.0	83.6	5.24
19E3		CH_3	144.8	277.0	132.2	4.52
19E5		C_3H_7	125.9	253.9	127.6	4.57
20		H	107.7	181.7	74.0	6.24
20E5		C_2H_5	85.1[g]	126.3	41.2	5.55
20Z5			81.9[h]	165.0	83.1	4.59
21		H	119.2	232.7	113.5	4.85
21E5		CH_3	124.1	242.6	118.5	5.72
22			77.4	200.8	123.4	3.95

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

[b] Crystal-nematic transition (m.p.).

[c] Nematic-isotropic transition. A monotropic transition temperature is denoted by () brackets around the recorded temperature.

[d] $\Delta T = T_{N-I} - T_{C-N}$ = mesorange; a negative sign indicates monotropy.

[e] Virtual clearing point determined in p-[2-(*trans*-4-pentylcyclohexyl)ethyl]phenyl ethyl ether (T_{N-I} = 47,0°C).

[f] Second modification melts at 16,8°C

[g] Smectic-nematic transition at 75,4°C.

[h] Smectic-nematic transition at 62,4°C.

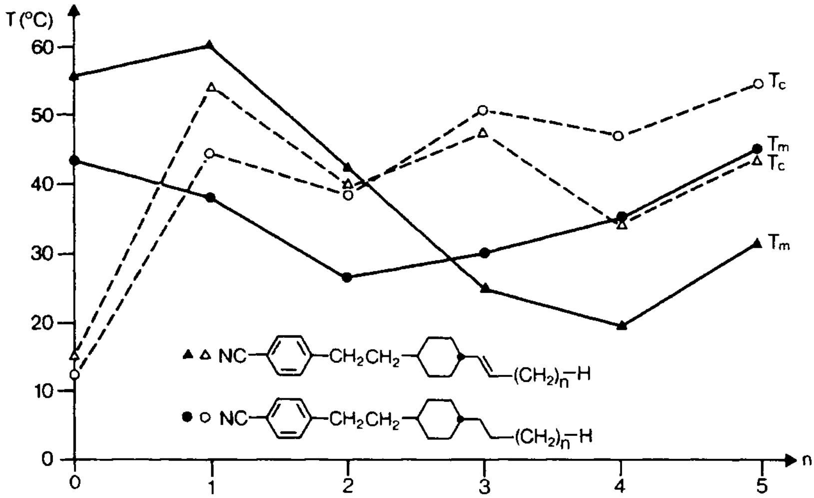


FIGURE 1 Comparison of the transition temperatures of 1-alkenylsubstituted cyanophenylethylcyclohexanes with those of their hydrogenated counterparts.

—Due to a relatively strong rise of the T_m-values the cyanophenylethylcyclohexanes with short side chains (n = 0,1,2) show only virtual or monotropic nematic behaviour and consequently exhibit less favorable mesoranges (T_c-T_m). The mesoranges of the other homologues (n = 3,4,5), however, are similar to those of the corresponding hydrogenated counterparts.

By insertion of additional methylene units between the vinyl and the cyclohexane moiety of *8* both the total length of the side chain and the position of the incorporated C,C-double bond are altered. The effect of such structural modifications on the transition temperatures is shown in Figure 2 and the following conclusions can be drawn:

—an extremely strong alternation of the T_c-values is observed, which is (i) much more pronounced than that of the correspondingly hydrogenated counterparts[5] 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.

—the melting points (T_m) are less affected and alternate on parallel lines to the T_c-values, albeit much less markedly.

Finally, both the melting and the clearing point are raised, if an *E*-olefin unit is shifted from the 1- to the 3-position within a side chain of defined molecular length (cf. *8E5* with *10E5* Table I).

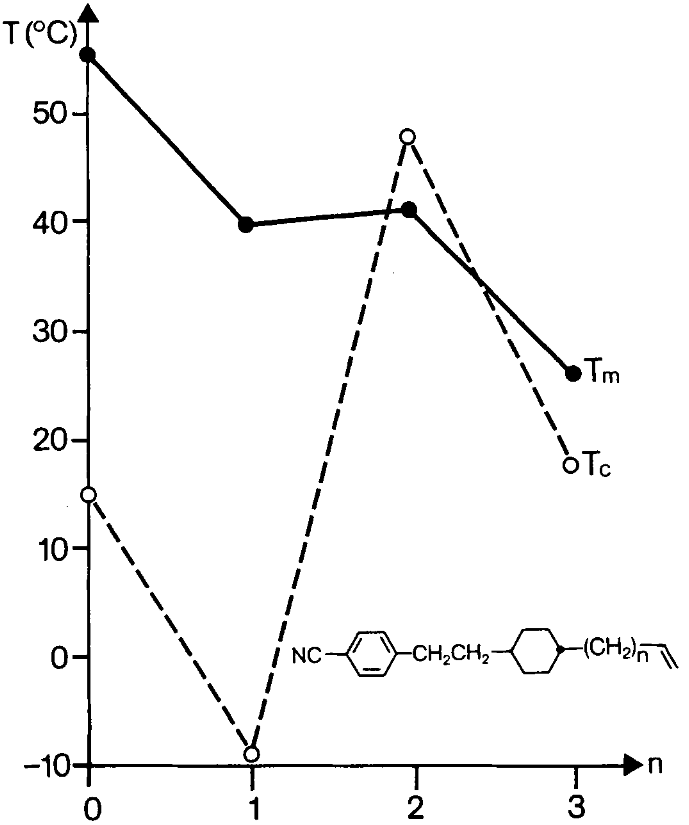


FIGURE 2 Transition temperatures of a homologous series of ω-alkenylsubstituted cyanophenylethylcyclohexanes.

In summary, the effects caused by insertion of isolated, *E*- or *Z*-configurated C,C-double bonds at various positions of the terminal side chains of cyanophenylethylcyclohexanes on the transition temperatures strongly parallel those observed previously in the PCH-series.[1]

Cyanobiphenylylcyclohexanes

Although some members of the homologous series of 1-*E*-alkenyl-substituted cyanobiphenylylcyclohexanes are missing (*cf.* Table I), a similar odd-even effect as in the formerly discussed ethane series may likewise be observed here, *i.e.* members with an even number of carbon atoms in the side chain (e.g. *19*) exhibit low T_c-values, whereas odd-membered nitriles (e.g. *19E3*, *19E5*) show high T_c-values. Again the short-membered representatives (e.g. *19*, *19E3*) are distinguished by their relatively high melting points. In the case of nitrile *19E5* a direct comparison with the corresponding saturated nitrile[6] (T_m = 94°C, T_c = 219°C, ΔT = 125°C) is possible. Accordingly both the melting and the clearing point of the former are raised by *ca.* 30–40°C.

The influence of the position of a C,C-double bond within terminal side chains of either varying or constant length is demonstrated in Figures 3 and 4.

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

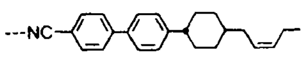
—In both series of compounds a strong alternation of the T_c-values is observed (Figures 3 and 4)

—In the case of ω-alkenylsubstituted cyanobiphenylylcyclohexanes (Figure 3) this alternation of the clearing points (T_c) is 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 and *vice versa*.

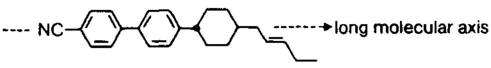
—The melting points (T_m) alternate in both series on parallel lines to the T_c-values, albeit less markedly (Figures 3 and 4).

By comparing 1-alkenyl- with 3-alkenylsubstituted cyanobiphenylylcyclohexanes of the same molecular length (*cf.* *19E5* with *21E5* in Table I) a lowering of both T_m and T_c is observed. This mesomorphic behaviour is opposite to that previously encountered in the corresponding series of both cyanophenylethylcyclohexanes (*cf.* *8E5* with *10E5* in Table I) and cyanophenylcyclohexanes (*cf.* Ref. 1).

Finally, the influence of the configuration of a C,C-double bond on the transition temperatures has been studied. Thus by comparing the mesomorphic properties of nitrile *20E5* with those of *20Z5* the considerably higher T_c-value of the latter attracts attention. This somewhat surprising result might possibly be explained by the better alignment of the alkenyl side chain of the *Z*-isomer *20Z5* along the molecular axis; in the case of *20E5* the optimal U-shape of the side chain cannot be adopted.



20 Z5



20 E5

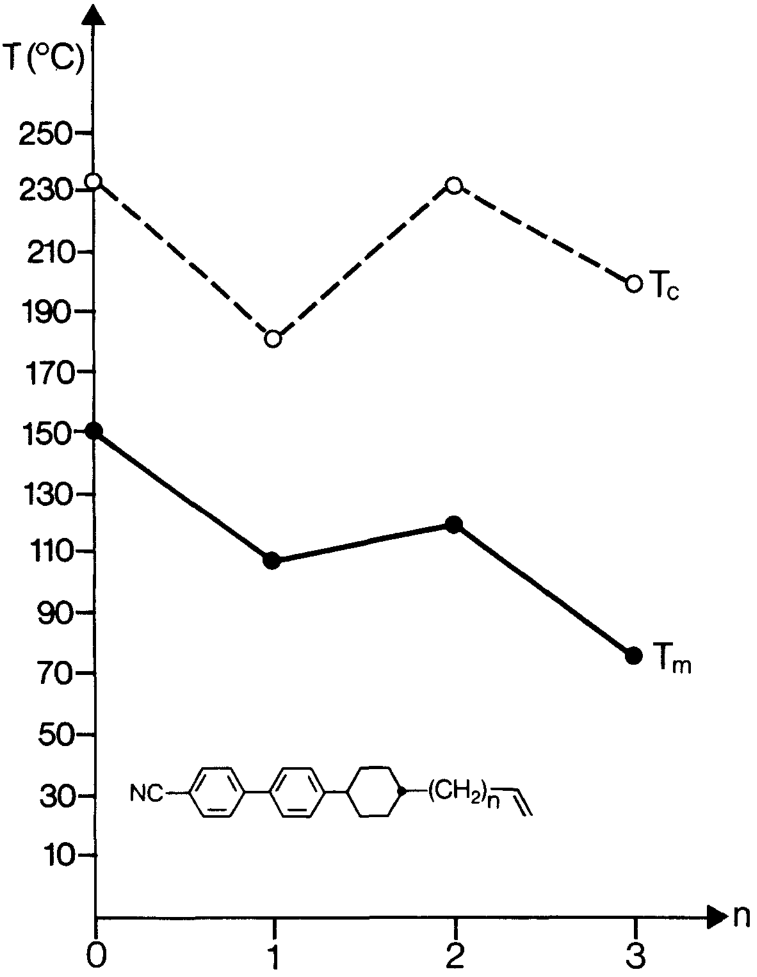


FIGURE 3 Transition temperatures of a homologous series of ω-alkenylsubstituted cyanobiphenylylcyclohexanes.

CONCLUSIONS

The replacement of a dimethylene unit by a C,C-double bond at different positions in the alkyl side chains of cyanophenylethylcyclohexanes and cyanobiphenylylcyclohexanes may substantially alter the mesomorphic properties of these systems. The resulting changes in the transition temperatures are strongly dependent on both the

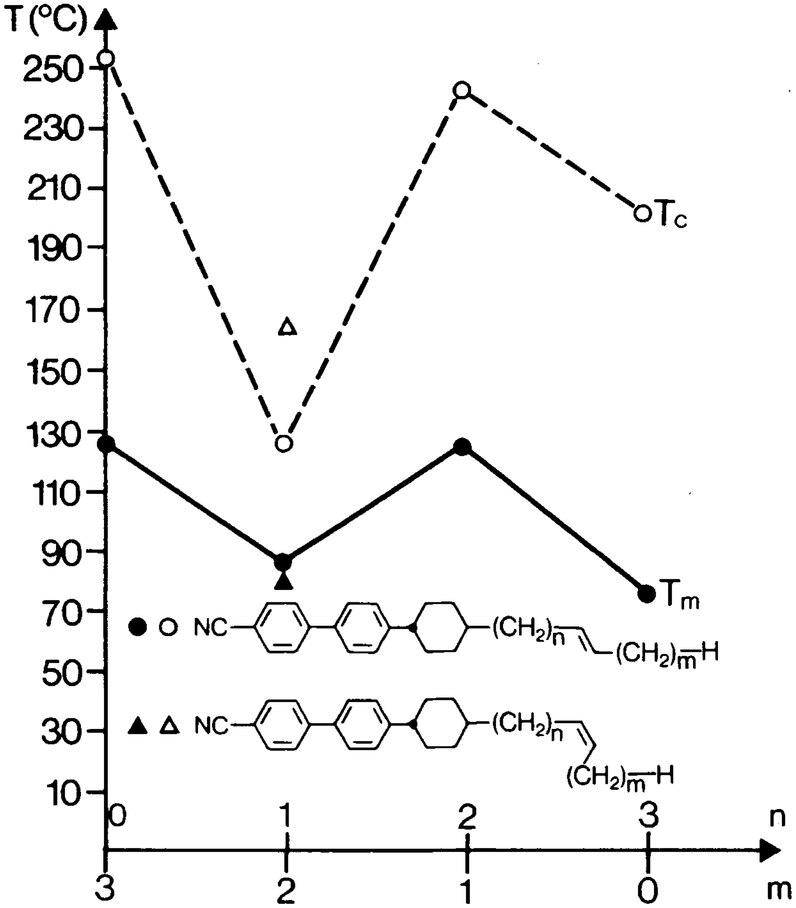


FIGURE 4 Transition temperatures of isomeric pentenylsubstituted cyanobiphenylylcyclohexanes.

position and the configuration of the inserted olefin units. In general they parallel those observed earlier in the PCH-series.[1]

Acknowledgments

We wish to thank Mr. G. Daub for his competent collaboration during the preparation of the new materials and Mr. F. Wild and B. Halm for carrying out the differential thermal analyses.

EXPERIMENTAL PART

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 I, 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% p-[*trans*-4-[2-[4'-(*trans*-4-pentylcyclohexyl)-4-diphenylyl]ethyl]cyclohexyl]benzonitrile at 5.0 bar N_2 and temperatures of 170–280°C (isotherm). All IR, ^{1}H-NMR and mass spectra of the new compounds are in agreement with their assigned structures.

Preparation of cyanoketone *3*

To a slurry of (methoxymethyl)triphenylphosphonium chloride (149g, 434 mmol) in dry *t*-butyl methyl ether (860 ml) at −10°C was added solid *t*-BuOK (51.6g, 460 mmol) over 10 min. After stirring an additional 30 min at 0° a solution of 1,4-dioxaspiro[4.5]decan-8-one *1*[2] (47.3g, 303 mmol) in dry THF (720 ml) was added over 45 min to the deep orange mixture. Stirring was continued for 2 h at RT before the reaction mixture was poured into hexane (5 l) and filtered through a pad of Celite. The solvents were removed *in vacuo* and the resulting yellow-brownish oil was again triturated with hexane (500 ml) and filtered. Flash chromatography of the concentrated filtrate (61.7 g) on silica gel (methylene chloride/acetone 98:2 and 95:5) afforded 8-(methoxymethylene)-1,4-dioxaspiro[4.5]decane (53.5g, 96%) as a colourless oil, TLC (methylene chloride/acetone 9:1): R_f 0.68.

This enol ether (28.2g, 153 mmol) was dissolved in a mixture of glacial acetic acid (770 ml) and water (385 ml) and heated to reflux for 1 h. Dilution with water (800 ml) and extraction with methylene chloride (3 × 700 ml) followed by washing the organic layers with 10% sodium carbonate solution and the usual work up gave a brown liquid (18.5 g), which upon flash chromatography on silica gel (methylene chloride) afforded 4-formylcyclohexanone *2* (16.5g, 85%) as a slightly brownish liquid. TLC (methylene chloride/acetone 9:1): R_f *(2)* 0.54.

To a slurry of 4-cyanobenzyltriphenyl-phosphonium chloride (63.3g, 153 mmol) in dry 1,2-dimethoxyethane (195 ml) was added solid *t*-BuOK (17.2g, 153 mmol) whereby the temperature rose to 44°C. After cooling the brown-orange suspension to 0°C a solution of aldehyde *2* (16.7g, 132 mmol) in dry 1,2-dimethoxyethane (100 ml) was added over 2 min. Stirring was continued for 3.5 h at RT before the reaction mixture was poured into water (500 ml). Extraction with methylene chloride (3 × 600 ml) followed by the usual work up furnished a brownish paste (76.9g), which upon flash chromatography on silica gel (methylene chloride) afforded a dark yellow oil (33.0g).

This material was dissolved in toluene/ethanol 2:1 (780 ml) and hydrogenated at normal pressure with 5% palladium-on-carbon (3.2g) until uptake of hydrogen ceased. Filtration and concentration *in vacuo* furnished a yellow oil, which upon flash chromatography on silica gel (methylene chloride/hexane 1:1, 8:2 and methylene chloride) and crystallization from *t*-butyl methyl ether afforded cyanoketone *3* (22.6g, 77%) as colourless crystals, m.p. 62.5–64.3°C. TLC (methylene chloride/acetone 9:1): R_f *(3)* 0.71.

Preparation of cyanoketone 14

To a solution of aluminum chloride (26.7g, 200 mmol) in dry 1,2-dichloroethane (200 ml) was added at RT a solution of 4-biphenylylcyclohexanone[3] *12* (50.0g, 200 mmol) in dry 1,2-dichloroethane (200 ml) over 10 min. The resulting fine, brown-violet suspension was then transferred at RT over 15 min *via* a steel tube into a brown suspension, previously generated by adding oxalyl chloride (34.2 ml, 400 mmol) to a solution of aluminum chloride (26.7g, 200 mmol) in dry 1,2-dichloroethane (400 ml) at RT over 5 min. A slightly exothermic reaction ensued, which produced a black suspension. After stirring for an additional 10 min the reaction mixture was cooled to −10°C, very carefully quenched with $CaCl_2$-solution (250 ml, 30%) (strongly exothermic) and washed with methylene chloride (4 × 1.5 l). The organic layers were washed with water (3 × 1 l), dried over $MgSO_4$ and concentrated to a volume of ca. 250 ml. The resulting solution was then added to cooled (15°C) and well-stirred 15% NH_4OH-solution (190 ml). A thick, cream-coloured precipitate was formed, which after being stirred for an additional 12 h was filtered off, washed thoroughly with water and dried at 80°C/12 mm for 12 h affording amide *13* (50.4g, 86%) as a cream-coloured powder. TLC (toluene/acetone 7:3): R_f (*13*) 0.14.

A mixture of amide *13* (67.1g, 230 mmol) and benzenesulfonyl chloride (91.5 ml, 710 mmol) in dry pyridine (345 ml) was stirred at 72°C for 1 h. During this time the initially cream-coloured suspension was transformed into a clear, dark brown solution, which was poured onto a mixture of ice (2 kg) and conc. HCl (416 ml). Extraction with methylene chloride (3 × 700 ml) followed by the usual work up gave a brown oil (88.7g), which upon flash chromatography on silica gel (hexane/methylene chloride 1:1 and methylene chloride) and crystallization from hexane/methylene chloride 5:1 (RT → 0°C) afforded cyanoketone *14* (47.4g, 76%) as yellow crystals, m.p.: 146.0 – 149.2°C. TLC (methylene chloride): R_f (*14*) 0.11.

Preparation of cyanoaldehydes *15*, *16*, *17*, *18*, *4*, *5*, *6* and *7*

To a slurry of (methoxymethyl)triphenylphosphonium chloride (85.1g, 250 mmol) in dry *t*-butyl methyl ether (500 ml) at −15°C was added solid *t*-BuOK (29.2g, 260 mmol) at once. After stirring for an additional 30 min at 0°C a solution of cyanoketone *14* (47.4g, 170 mmol) in dry THF (610 ml) was added over 15 min to the deep-orange mixture. Stirring was continued for 2.75 h at RT before the dark brown reaction mixture was poured into hexane (4 l) and filtered through a pad of Celite. Flash chromatography of the concentrated filtrate on silica gel (hexane/methylene chloride 1:1) and crystallization from hexane/methylene chloride 7:3 afforded the Wittig product (42.3g, 81%) as colourless crystals, m.p.: 118–118.9°C. TLC (methylene chloride): R_f 0.45.

The resulting enol ether (42.3g, 140 mmol) was dissolved in 2N HCl/THF 1:4 (260 ml) and heated to reflux for 30 min. Dilution with water (500 ml) and extraction with methylene chloride (3 × 300 ml) followed by the usual work up gave colourless crystals (40.5g), consisting (VPC) of a 5:1 *trans*/*cis*-mixture of epimeric cyanoaldehydes. Double crystallization of this material from methylene chloride/hexane afforded *trans*-cyanoaldehyde *15* (24.7g, 61%) as colourless crystals, m.p. 145.7°C (purity according to VPC: 98.6%). TLC (methylene chloride): R_f (*15*) 0.32.

By repeating the above procedure once, twice or three times, *15* was converted into the homologous cyanoaldehydes *16*, *17* and *18*, respectively, in yields of 71–90%.

Similarly cyanoketone *3* was converted into the cyanoaldehydes *4* (m.p. 90.0–91.2°C), *5*, *6* and *7*, respectively, in comparable yields.

Preparation of ω-alkenylsubstituted nitriles *22*, *19*, *20*, *21*, *8*, *9*, *10* and *11*

To a slurry of methyltriphenylphosphonium bromide (3.5g, 9.9 mmol) in dry *t*-butyl methyl ether (20 ml) at −10°C was added solid *t*-BuOK (1.2g, 10.5 mmol) at once. After stirring for an additional 30 min at −10°C a solution of cyanoaldehyde *18* (2.3g, 6.9 mmol) in dry THF (17 ml) was added over 30 min to the yellow mixture. Stirring was continued for 2 h at RT before the reaction mixture was poured into hexane (680 ml) and filtered through a pad of Celite. Flash chromatography of the concentrated filtrate (3.7 g) on silica gel (hexane/methylene chloride 7:3) and crystallization from methylene chloride/hexane produced nitrile *22* (1.69 g, 75%) as colourless crystals. TLC (methylene chloride): R_f (*22*) 0.58.

Following the above procedure the aldehydes *15*, *16*, *17*, *4*, *5*, *6* and *7* were converted into the nitriles *19*, *20*, *21*, *8*, *9*, *10* and *11*, respectively, in comparable yields.

Preparation of the *Z* cyano-olefin *20Z5*

To a slurry of propyltriphenylphosphonium bromide (5.91g, 15.3 mmol) in dry *t*-butyl methyl ether (68 ml) at RT, solid *t*-BuOK (1.77 g, 15.3 mmol) was added at once. After stirring for an additional hour at RT, a solution of aldehyde *16* (3.08g, 10.2 mmol) in dry THF (42 ml) and dry *t*-butyl methyl ether (25 ml) was added over 15 min to the cooled (−55°C) deep-orange mixture. Stirring was continued for 1.5 h at −30°C before the reaction mixture was poured into hexane (200 ml) and filtered through a pad of Celite. Flash chromatography of the concentrated filtrate (5.2g) on silica gel (hexane/methylene chloride 1:1) gave colourless crystals (2.93g). According to VPC-analysis, this material contained *20Z5* (83.5%) and *20E5* (3.0%) (*20Z5*:*20E5* = 96:4). Three crystallizations from ether/hexane produced pure nitrile *20Z5* (0.99 g, 29.4%, purity according to VPC: 99.5%) as colourless crystals. TLC (hexane/ethyl acetate 9:1): R_f (*20Z5*): 0.65.

Following the above procedure, the aldehydes *15*, *17*, *4* and *6* were converted to *19Z3*:*19E3* = 88:12, *19Z5*:*19E5* = 96:4, *21Z5*:*21E5* = 92:8, *8Z3*:*8E3* = 94:6, *8Z4*:*8E4* = 97:3, *8Z5*:*8E5* = 97:3, *8Z6*:*8E6* = 97:3, *8Z7*:*8E7* = 97:3 or *10Z5*:*10E5* = 92:8, in comparable yields. These mixtures then served as starting materials for the preparation of the corresponding pure *E*-isomers as described in the following experiments.

Preparation of the *E* cyano-olefins *19E5*, *19E3*, *20E5*, *21E5*, *8E3*, *8E4*, *8E5*, *8E6*, *8E7* and *10E5*

To a mixture of *m*-chloroperbenzoic acid (85%, 10.3g, 50.7 mmol) and powdered potassium carbonate (19.2g, 139 mmol) in dry methylene chloride (200 ml) at RT, a solution of a mixture of cyano-olefins *19Z5*:*19E5* = 96:4 (16.7g, 50.7 mmol) (cf. preceding experiment) in dry methylene chloride (180 ml) was added over 15 min. After stirring for an additional 30 min more *m*-chloroperbenzoic acid (85%, 5.15g, 25.4 mmol) was added. Then the heterogeneous reaction mixture was stirred for another 2 h at RT before it was poured into sodium thiosulfate solution (10%, 310 ml). Extraction with methylene chloride (1 × 200 ml), followed by washing the organic layers with sat. sodium carbonate solution and the usual work up, furnished a mixture of epoxides *23a*:*23b* = 4:96 (18.2g, 104%) as colourless crystals. TLC (methylene chloride): R_f (*23a*, *23b*) 0.29.

To a solution of triphenylphosphine (16.5g, 62.9 mmol) in dry methylene chloride (215 ml) 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 dried, solid residue suspended in dry toluene (215 ml). To this was added a solution of the epoxides *23a*/*23b* (18.2g) in dry toluene (130 ml) and the reaction mixture was heated to reflux for 2.5 h. Flash chromatography of the concentrated reaction mixture on silica gel (toluene) gave colourless crystals (24.2g), which after two crystallizations from methylene chloride/hexane produced analytically pure *erythro*-dibromide *24a* (20.2g, 81%) as colourless crystals with T_{C-N}: 157.2 − 157.6°C and T_{N-I}: 166.5 − 166.7°C. TLC (methylene chloride): R_f (*24a*) 0.60.

To a solution of the *erythro*-dibromide *24a* (20.2g, 41.3 mmol) in glacial acetic acid (700 ml) at RT, zinc dust (34.7g, 531 mmol) was added at once (slightly exothermic). After stirring for an additional 1.5 h at RT, the reaction mixture was poured into water (4.7 l). Extraction with petroleum ether/methylene chloride 4:1 (3 × 2 l), followed by washing the organic layers with sat. sodiumcarbonate solution (2 × 1.5 l) and the usual work up, gave colourless crystals (13.3g), which after crystallization from methylene chloride/methanol (RT → 0°C) produced nitrile *19E5* (12.7 g, 93%) as colourless crystals (purity according to VPC > 99.9%). TLC (hexane/ethyl acetate 9:1): R_f (*19E5*) 0.35.

Following the above procedures the cyano-olefins *19E3*, *20E5*, *21E5*, *8E3*, *8E4*, *8E5*, *8E6*, *8E7* and *10E5* were obtained in comparable yields. Purification by crystallization occurred either at the stage of the corresponding *erythro*-dibromides or was applied only to the final *E*-olefins. In the latter case the crude mixtures of dibromides were carried through the following zinc reduction.

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