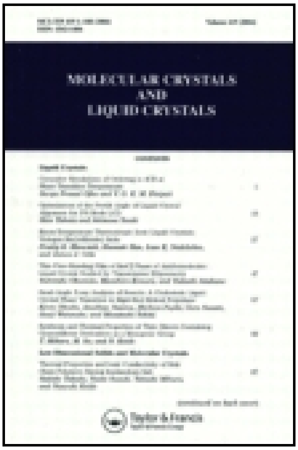

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Polar Acetylenic Liquid Crystals with Broad Mesomorphic Ranges. The Positional Influence of Different C, C-Elements on the Transition Temperatures

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Polar Acetylenic Liquid Crystals with Broad Mesomorphic Ranges. The Positional Influence of Different C,C-Elements on the Transition Temperatures†

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Various mesogenic nitriles with inserted dimethylene, *trans*-vinylene and especially ethynylene units at different positions in the structures of typical nematogens have been prepared and examined with regard to their transition temperatures. The thermal stabilities of the mainly nematic phases for these new compounds were compared with those for the corresponding nitriles lacking these *C*, *C*-elements. Nematic thermal efficiency orders are given.

INTRODUCTION

Although a number of guidelines exist which allow predictions to be made to some extent about various physical properties of newly devised liquid crystal materials, there are still many exceptions to these so-called rules. Nevertheless, by preparing new liquid crystal materials which differ only by a single structural element with regard to a known compound, old "rules" may either be confirmed or new ones may be established. It is the aim of this study to contribute to this type of structure-property relationship by specifically investigating the influence of dimethylene, *trans*-vinylene and ethynylene ele-

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†Presented at the 13th Freiburger Arbeitstagung Flüssigkristalle, Freiburg i.Br., Germany, March 23–25, 1983.

ments inserted at various positions in the structures of classical nematogens on the transition temperatures. Due to the sparse occurrence of acetylenic liquid crystal materials, a number of these compounds, as well as some other members of the dimethylene and *trans*-vinylene series, had to be prepared. This was accomplished by using various synthetic strategies and standard methodologies; however, for reasons of clearness these are not discussed in this communication†. To simplify matters, only bicyclic‡ derivatives substituted with a **n**-pentyl side chain are taken into consideration.

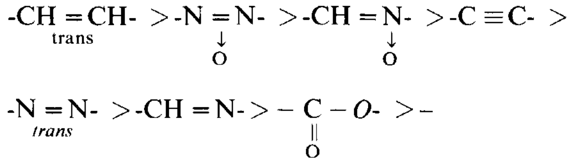
RESULTS AND DISCUSSION

Whereas the behaviour of the melting points (T_m) of liquid crystal materials is generally difficult to predict due to the often unknown packings of the molecules, more reliable statements can be made with regard to the clearing points (T_c). Broadly speaking, both transition temperatures are a function of the anisotropy of molecular polarizability and/or of the anisotropy of molecular shape.

Thus it is generally accepted that the molecule of a liquid crystal material is composed of a central rigid core and two terminal side chains, which may be of a polar or an apolar nature. In the case of bicyclic compounds, the rigid core may consist of two ring systems, which are linked to each other either by a covalent bond or by a two-atomic bridging group *X*. In LC-classes containing only phenylene ring systems, the average efficiency of both, the polar substituent

Z: $\mathrm{CN > OCH_3 > NO_2 > Cl > Br > N(CH_3)_2 > CH_3 > F > H}$

X:



$$\underset{\text{trans}}{\text{-CH=CH-}} > \text{-N}\underset{\substack{\downarrow\\ \text{O}}}{=}\text{N-} > \text{-CH=}\underset{\substack{\downarrow\\ \text{O}}}{\text{N}}\text{-} > \text{-C}\equiv\text{C-} >$$

$$\underset{\textit{trans}}{\text{-N=N-}} > \text{-CH=N-} > -\underset{\substack{\|\\ \text{O}}}{\text{C}}-\textit{O}\text{-} > -$$

---

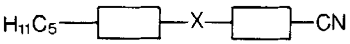
† For part of the experimental results see Ref. 1.

‡ The word bicyclic refers in this communication to compounds, which contain two six-membered rings (C_6H_4 or C_6H_{10}).

Z and the linking unit X in increasing N-I transition temperatures is known[2] and corresponds approximately to the sequence shown above. In the following work, special attention is paid to the cyano group as the polar end group Z and to the dimethylene, *trans*-vinylene and ethynylene elements as linking units or as part of polar or apolar side chains.

Variation of the core linking unit

This section covers bicyclic nitriles of the general structure shown below



$$X: \quad -, -CH_2-CH_2-, \underset{\text{trans}}{-CH=CH-}, -C\equiv C-$$

To start with we were interested in learning something about the influence of an inserted dimethylene bridge on the transition temperatures. In contrast to the known directly linked systems *1*, *3*, *5* and *7* (Table I), in the dimethylene series, three out of the four members of interest had to be synthesized (*2*, *6* and *8*). The transition temperatures of all these compounds are listed in Table I. By comparing these data, the following conclusions can be drawn:

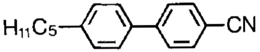
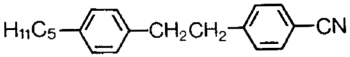
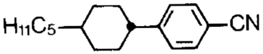
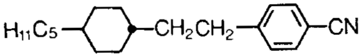
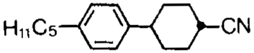
a) With the exception of nitrile *2*, all other dimethylene nitriles *4*, *6* and *8* show similar melting and somewhat lower clearing points in comparison with the corresponding directly linked systems *1*, *3*, *5* and *7*. The slight decrease of the T_c-values most probably reflects the more flexible cores of the dimethylene derivatives.

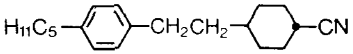
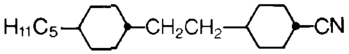
b) A remarkable drop in the clearing point is observed if the ring moieties in the phenylcyclohexyl systems *3* and *4* are reversed, leading to *5* and *6* respectively. A convincing explanation for this phenomenon occurring in both series is still lacking.

c) Nitrile *2* exhibits a surprisingly low virtual clearing point, thus representing the only irregularity within this series. In addition to a possibly unfavourable molecular pairing,[4] adoption of conformation *B* rather than *A* could account for this very low T_c-value. In contrast to *A*, conformation *B* provides an additional double σ-π overlap between the σ-orbitals of the central C,C-single bond and the adjacent p-orbitals of the benzene rings.

TABLE I

The influence of a dimethylene bridge on the transition temperatures of bicyclic nitriles[a]

No	Compounds	T_m	T_c	T_c-T_m	S/N	ΔT_c	ΔT_c-T_m	Lit.[b]/remarks
1		22,5	34,8	12,3	N			3
						– 58,8	– 97,9	
2		61,6	[–24]	– 85,6				this work, 4
3		30	55	25	N			5
						– 2,5	– 3,4	
4		30,9	52,5	21,6	N			4
5		16	[–25]	– 41				6
						15,0	8,6	

6		22,4	(−10,0)	−32,4	N			
7		62	85	23	S/N			7, $T_{S\text{-}N} = 52$
						−12,3	9,4	
8		40,3	72,7	32,4	S/N			$T_{S\text{-}N} = 56,5$

[a] The following abbreviations are used in Tables 1–6:

T_m = melting point (°C)

T_c = clearing point (°C, a monotropic transition temperature is denoted by a ( ) bracket around the recorded temperature, whilst a virtual value is signified by a [ ] bracket.

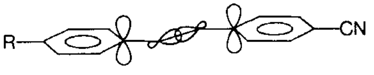
T_c-T_m = meso-range; a negative sign indicates monotropy.

S/N = mesomorphic behaviour (S = smectic, N = nematic)

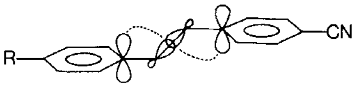
ΔT_c = Difference in clearing points of two compounds; a positive sign denotes a higher clearing point for the compound listed on top and *vice versa*.

ΔT_c-T_m = Difference in meso-ranges of two compounds; a positive sign denotes a broader mesorange for the compound listed on top and *vice versa*.

[b] If no reference is given, the indicated results originate from this work. For polymorphic compounds, the smectic-nematic transition temperatures ($T_{S\text{-}N}$) are listed in this row.



a



b

To study the influence of unsaturation in the linking *C,C*-elements, the two unknown nitriles *11* and *12* in the diphenyl and phenylcyclohexyl series were prepared (cf. Table II).

In both series, the following nematic thermal efficiency order may be compiled for the linking units examined:

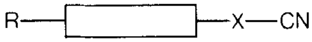
$$\text{-CH} = \text{CH-} > \text{-C} \equiv \text{C-} > \text{-CH}_2\text{-CH}_2\text{-}$$

The markedly higher T_c-values of the unsaturated nitriles *10* and *12* in comparison with those of the acetylenic counterparts *9* and *11* is somewhat surprising. According to molecular models, the latter seem to be better disposed for alignment in the nematic phase due to the rigid nature of the *C,C*-triple bond.

In general, members of the phenylcyclohexyl series exhibit lower melting points than the corresponding diphenyl systems, thus supplying these compounds with broader mesophase ranges.

Variation of the polar end group

Besides the central core, both terminal chains may in principle be altered in a similar way. This section covers nitriles of the general structure shown below.



$$X\text{:}\quad \text{-CH}_2\text{-CH}_2\text{-}, \text{-CH} = \text{CH-}, \text{-C} \equiv \text{C-}$$

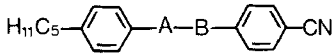
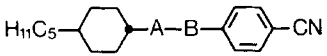
To begin with, we chose to investigate the influence of the indicated *C,C*-elements on the mesogenic properties of members of the biphenyl, phenylcyclohexyl and phenylcyclohexylethyl series. Accordingly, with the exception of the known nitriles *13* and *16*, all missing compounds required for a direct comparison were synthesized using standard methods. Their transition temperatures are listed and compared with those of the corresponding benzonitriles *1*, *3* and *4* in the following Table III.

Several comments on these data seem to be worthwhile.

a. Propiononitriles (13–15). Unlike the only known nitrile *13*[10] in this series, the newly prepared representatives *14* and *15* showed liquid crystalline properties. The exclusively smectic behaviour most probably originates from the interruption of the conjugated systems

TABLE II

The influence of different *C*, *C*-bridging elements on the transition temperatures of bicyclic nitriles[a]

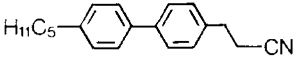
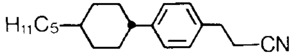
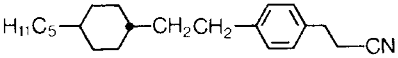
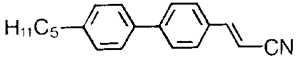
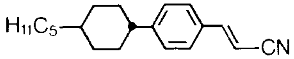
No.	Compound	A − B	T_m	T_c	T_c-T_m	S/N	Lit/remarks
9		C ≡ C	79, 5	(70, 5)	(−9, 0)	N	8
10		C = C	55, 5	101	45, 5	N	9
2		C − C	61, 6	[−24]	− 85, 6		this work, 4
11		C ≡ C	41, 4	72, 5	31, 1	N	
12		C = C	38, 7/53, 5[b]	107, 2	53, 7	N	
4		C − C	30, 9	52, 5	21, 6	N	4

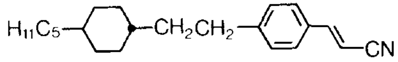
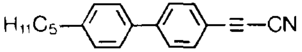
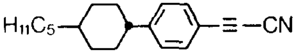
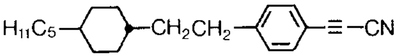
[a] For the abbreviations used and additional remarks see Table I, footnotes a and b.

[b] Different crystalline modifications were observed. For the estimation of the meso-ranges T_c-T_m , the higher melting points (T_m) were taken.

TABLE III

The influence of different *C*, *C*-elements inserted into the polar end groups of bicyclic nitriles on the transition temperatures[a]

No.	Compounds	T_m	T_c	T_c-T_m	S/N	ΔT_c[b]	ΔT_c-T_m[b]	Lit./remarks
13		66,5	-	-	-	-	-	10
14		44,2	(28,0)	− 16,2	S	− 27,0	− 41,2	
15		25,2	53,2	28	S	0,7	6,4	
16		80	147,1	67,1	S/N	112,3	54,8	$T_{S\text{-}N} = 99,11$
17		40,6	149	108,4	S/N	94,0	83,4	$T_{S\text{-}N} = 59,5$

18		64,4	129	64.6	S/N	76,5	43,0	$T_{S\text{-}N}$ = 101,0
19		51.0	120,2	69,2	N	85,4	56,9	
20		49,7	128,9	79,2	N	73,9	54,2	
21		36,7	105,5	68,8	N	53,0	47,2	

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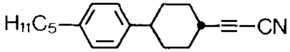
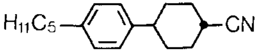
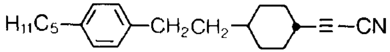
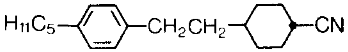
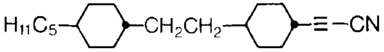
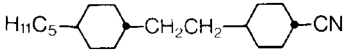
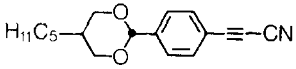
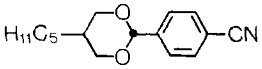
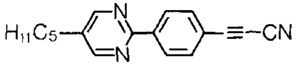
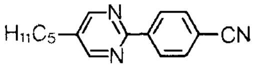
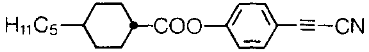
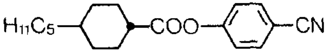
[a] For the abbreviations used and additional remarks see Table I, footnotes a and b.

[b] These values refer to a comparison with the corresponding benzonitriles *1*, *3*, and *4*. For the structure and transition temperatures of these compounds cf. Table I.

TABLE IV

The influence of ethynylene elements inserted into the polar end groups of various other classes of liquid crystal materials on the transition temperatures[a]

No.	Compounds	T_m	T_c	T_c-T_m	S/N	ΔT_c	ΔT_c-T_m	Lit./remarks
22		46,9	(45,4)	− 1,5	N	70,4	39,5	
5		16	[−25]	− 41				6
23		36,5	43,0	6,5	N	53,0	38,9	
6		22,4	(−10,0)	− 32,4	N			
24		51,4	112,7	61,3	N	40	28,9	
8		40,3	72,7	32,4	S/N			$T_{S\text{-}N} = 56{,}5$

25		60,3	111,0	50,7	N	63,1	59,2	
26		56,4	(47,9)	−8,5	N			12
27		76,2	128,5	52,3	N	76,5	70,8	
28		70,5	(52,0)	−18,5	N			13
29		76,8	153,5	76,7	N	74,5	44,7	
30		47	79	32	N			14

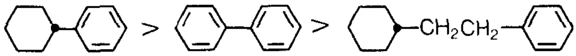
[a] For the abbreviations used and additional remarks see Table I, footnotes a and b.

by the inserted dimethylene units, thereby decreasing the anisotropy of molecular polarizability considerably.

In contrast to observations made earlier (cf. *3* with *4* in Table I, *17* with *18*, and *20* with *21* in this table), the phenylcyclohexylethyl system *15* exhibits a substantially higher T_c-value than the corresponding phenylcyclohexyl derivative *14*. We do not dare to give an explanation for this surprising result.

b. Cinnamonitriles (16–18). The three substituted cinnamonitriles *16–18* attract attention by their particularly high clearing points. In comparison with the benzonitriles *1*, *3* and *4*, insertion of a *trans* double bond in these cases causes elongation of both the conjugated systems and the molecules themselves leading to an increase in thermal stability of the nematic order. As a consequence, nematogens result with extremely large meso-ranges, which however, due to a photochemically induced *trans/cis*-isomerization of the double bonds, are also very UV-labile and therefore cannot be used in practice.[11]

c. Propiolonitriles (19–21). To our knowledge, none of these compounds is described in the literature, and therefore we prepared the three representatives *19–21* (Table III) by standard methods. With respect to the clearing points, similar trends were observed as in the series of the cinnamonitriles. Although their $T_{N\text{-}I}$-values are about 20°C lower than those of the above mentioned nitriles *16–18*, these purely nematic compounds still show attractive meso-ranges in the order of 70–80°C! Within both the cinnamonitrile and the propiolonitrile series, the following nematic efficiency order results for the three central core systems studied:



We are now in a position to study the influences which different *C,C*-elements, if connected to cyano end groups, exert on the transition temperatures of members of three classes of liquid crystals (biphenyls, phenylcyclohexanes and phenylcyclohexylethanes). From the data given in Table III the following conclusions can be drawn:

a) The thermal efficiency order of the mesophases is the same in all three classes investigated:

$$\text{-CH}=\text{CH-} > \text{-C}\equiv\text{C-} \gg \text{-CH}_2\text{-CH}_2\text{-}$$

b) With the exception of the members of the phenylcyclohexyl series, the meso-ranges diminish in the order

$$\text{-C} \equiv \text{C-} > \text{-CH} = \text{CH-} > \text{-CH}_2\text{-CH}_2\text{-}$$

c) The tendency to form nematic phases decreases in the order

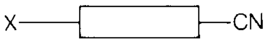
$$\text{-C} \equiv \text{C-} > \text{-CH} = \text{CH-} > \text{-CH}_2\text{-CH}_2\text{-}$$

d. Various other acetylenic nitriles. Having found a structural element which causes considerable broadening of purely nematic mesophase ranges and which, in contrast to conjugated 1,2-disubstituted double bonds, exhibits remarkable UV-stability, the question arose as to whether this principle could be generalized and thus transferred to other well-known classes of liquid crystals. Accordingly we prepared a number of other polar acetylenes, which will be discussed in this section. These compounds are listed in Table IV and were compared, with respect to their transition temperatures, with the corresponding systems lacking the ethynylene bridge.

As for the benzonitrile systems (cf. Table III), insertion of an acetylene unit into the polar end group leads to a strong increase in the $T_{\text{N-I}}$-values (40–75°C) and accordingly to a considerable broadening of the meso-ranges (30–70°C). Thus, compounds exhibiting only virtual clearing points (e.g. *5*) become weakly monotropic, and monotropic liquid crystals (e.g. *6*, *26* and *28*) become enantiotropic. Although it is not the purpose of this publication to discuss physical properties other than transition temperatures[†], it should be mentioned at this point, that properties, which are typical for certain classes such as the low optical anisotropy for nitrile *6*, the high dielectric anisotropy for cyanopyrimidine *28* or the ability of dioxan *26* to induce low threshold voltages in mixtures are very little affected by the introduction of an acetylene unit.

Variation of the apolar terminal chain of substituted benzonitriles

Finally, the possibility of an analogous variation of the apolar terminal chain in substituted benzonitriles remained to be investigated. To get an idea of the transition temperatures which are

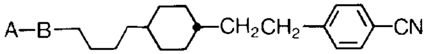


$X = \text{–CH}_2\text{–CH}_3, \text{–CH=CH}_2, \text{–C}\equiv\text{CH}$

[†] Additional physical properties of the new acetylenic liquid crystal materials will be discussed elsewhere.

TABLE V

The influence of different *C*, *C*-elements inserted into the apolar side chains of cyclohexylethyl benzonitriles on the transition temperatures[a]

No.	Compound	A – B	T_m	T_c	T_c-T_m	S/N	Lit./remarks
31		C≡C	62,5	-	-	-	
32		C=C	25,3	(17,2)	–8,1	N	
4		C–C	30,9	52,5	21,6	N	4

[a] For the abbreviations used and additional remarks see Table I, footnotes a and b.

connected with such structural changes, we have prepared one representative each with a terminal alkene and acetylene unit in the phenylcyclohexylethyl series (Table V). If compared with the known nitrile *4*, it soon becomes apparent, that introduction of alkene or acetylene elements in this position leads to a considerable regression of the mesomorphic properties. Thus, nitrile *32* shows only monotropic behaviour, whereas nitrile *31* exhibits no mesogenic properties at all.

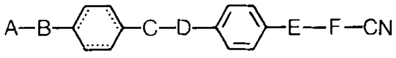
Positional influences of different *C*, *C*-elements

Making use of the transition temperatures of the known nitriles *4*, *9*, *33* and *34*, it is now possible to compare nitrile systems *of the same length*, which differ only in the position of the three *C*, *C*-elements in question (Table VI). In three out of four series examined (*17*, *12*, *32*/*19*, *9*, *34*/*20*, *11*, *31*), the T_c-values as well as the meso-ranges clearly decrease when the alkene or acetylene unit is moved away from the polar cyano end group. However, if a dimethylene unit is allowed to migrate correspondingly (*14*, *4*, *33*), exactly the contrary is observed. The further away from the cyano group, the less affected are the clearing points.

CONCLUSIONS

Introduction of dimethylene, *trans*-vinylene or ethynylene elements at different positions of bicyclic benzonitriles leads to the following nematic (smectic) thermal efficiency orders:

Insertion of *C*, *C*-triple bonds into polar cyano end groups *in general* causes a strong increase in clearing points and thus broadening of the meso-ranges.



$\text{A–B: C–C} > \text{C=C} > \text{C≡C}$

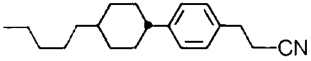
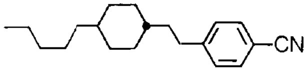
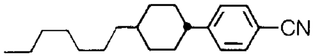
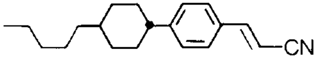
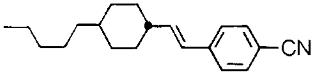
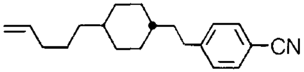
$\text{C–D: C=C} > \text{C≡C} > \text{C–C}$

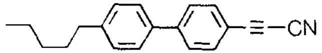
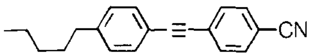
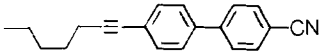
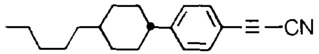
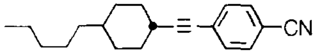
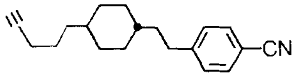
$\text{E–F: C=C} > \text{C≡C} \gg \text{C–C}$

A possible explanation of some of the observed orders based on molecular pairing arguments will be discussed elsewhere.

TABLE VI

The positional influence of different *C*, *C*-elements on the transition temperatures of various bicyclic nitriles[a]

No.	Compounds	T_m	T_c	T_c-T_m	S/N	Lit./remarks
14		44,2	(28,0)	− 16,2	S	
4		30,9	52,5	21,6	N	4
33		30	57	27	N	5
17		40,6	149	108,4	S/N	$T_{S\text{-}N} = 59,5$
12		38,7/53,5[b]	107,2	53,7	N	
32		25,3	(17,2)	− 8,1	N	

19		51	120,2	69,2	N	
9		79,5	(70,5)	−9	N	8
34		51,6	(49,1)	−2,5	N	15
20		49,7	128,9	79,2	N	
11		41,4	72,5	31,1	N	
31		62,5	-	-	-	

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[a] For the abbreviations used and additional remarks see Table 1, footnotes a and b.

[b] Different crystalline modifications were observed. For the estimation of the meso-range T_c-T_m, the higher melting points (T_m) were taken.

EXPERIMENTAL PART

The new products investigated were shown to be $> 99\%$ pure by various techniques (tlc, glc, thermoanalysis). Their transition temperatures (cf. tables I–VI) were determined using a *Mettler* DTA TA 2000 and are corrected.

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