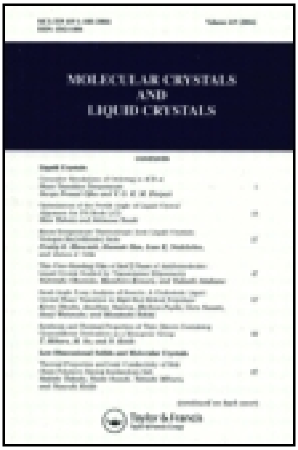

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Apolar Acetylenic Liquid Crystals

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Apolar Acetylenic Liquid Crystals

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A large number of bicyclic[†], apolar, acetylenic mesogens with the *C, C*-triple bond situated either in the central core unit or in the terminal chains have been synthesized. Where possible, their nematic or smectic thermal stabilities are compared with those of the corresponding dimethylene-bridged analogs.

INTRODUCTION

In the preceeding communication[1], we reported acetylenic nitriles as purely nematic liquid crystals with attractive meso-ranges. It was found, that insertion of a *C, C*-triple bond into the core or especially in the polar end group leads in general to nematogens with remarkably enhanced $T_{N\text{-}I}$-values whereas other typical properties remain more or less unaffected.

Bearing in mind that apolar liquid crystals usually exhibit lower viscosities than their polar counterparts, the question arose as to whether introduction of acetylene units into such systems would give a similar result with regard to transition temperatures. To answer this question, we needed a substantial number of acetylenic analogs of typical apolar mesogens such as phenylcyclohexanes (PCH), phenylcyclohexylethanes (PECH), esters etc . . . Since, with the exception of tolanes, virtually nothing is known from the literature about such compounds, all of the acetylenes, as well as many of the corresponding dimethylene analogs[‡] listed in Tables I–V have been prepared[§].

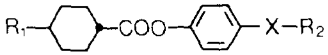
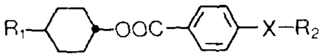
[†] The word bicyclic refers in this communication to compounds, which contain two six-membered rings (C_6H_4 or C_6H_{10}).

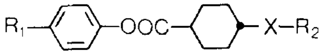
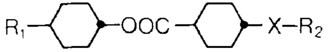
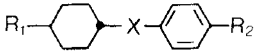
[‡] These reference compounds have been prepared by hydrogenation of the corresponding acetylenes.

[§] For part of the experimental results see Ref. 1b.

TABLE I

Comparison of the transition temperatures of acetylenic bicyclic esters with those of their hydrogenated counterparts[a]

			X: $C\equiv C$					X: CH_2-CH_2				
Compound	R_1	R_2	No.	T_m	T_c	T_c-T_m	S/N	T_m	T_c	T_c-T_m	S/N	Lit.[b,c] remarks
	C_5H_{11}	H	**1**	50,6	78,5	27,9	N	42,0	(29,0)	−13,0	N	2
	C_3H_7	CH_3	**2**	82,8	92,1	9,3	N	33,2	(30,4)	−2,8	N	3
	C_4H_9	CH_3	**3**	50,2	89,0	38,8	N	26,3	(23,1)	−3,2	N	
	C_5H_{11}	CH_3	**4**	80,0	99,3	19,3	N	44,0	(43,0)	−1,0	N	3
	C_4H_9	C_2H_5	**5**	50,1	58,2	8,1	N	24,9	(19,0)	−5,8	N	
	C_4H_9	C_3H_7	**6**	41,4	50,5	9,1	N	33,3	34,1	0,8	N	
	C_3H_7	CH_3	**7**	77,4	(73,4)	−4,0	N					
	C_4H_9	CH_3	**8**	79,8	(66,5)	−13,3	N	12,7	(−1,0)	−13,7	N	
	C_5H_{11}	CH_3	**9**	93,3	(76,1)	−17,2	N	33,0	[11,0]	−22		

	C_6H_{13}	H	**10**	49,8	(34,5)	− 15,3	N	22,0	45,0	13,0	N	2
	C_5H_{11}	H	**11**	54,2	(40,5)	− 13,7	N	20,5	35,0	14,5	S	4
	C_3H_7	C_3H_7	**12**	32,6	[−42,6]	− 75,2		24,0	52,5	28,5	S/N	4; $T_{S\text{-}N} = 37,5$
	C_5H_{11}	$COOCH_3$	**13**	67,0	74,3	7,3	N	36,8	48,7	11,9	N	5
	C_5H_{11}	$OOCCH_3$	**14**	66,3	(46,2)	− 20,1	N	41,5	(40,5)	− 1,0	N	6

[a] Abbreviations used in Tables 1–5
T_m = melting point (°C)
T_c = clearing point (°C, a monotropic transition temperature is denoted by ( ) 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)

[b] If no reference is given, the indicated results originate from this work.

[c] For polymorphic compounds, the smectic-nematic transition temperatures ($T_{S\text{-}N}$) are listed in this row.

For simplification only bicyclic acetylenes are taken into consideration; in the following text, these are divided into five classes. As a rule, the ethynylene unit may be (part of) a terminal end group or constitute the linking element of two six-membered ring systems. Tolanes are excluded.

1. ACETYLENIC ESTERS

Table I summarizes the results obtained from the newly prepared compounds. Where known the transition temperatures of the corresponding hydrogenated esters have been included. Within the series of *p*-1-alkynylphenol esters (*1–6*), all members exhibit enantiotropic nematic behaviour. In all cases, a direct comparison with the corresponding hydrogenated esters (CH_2-CH_2 linked) demonstrates that here the replacement of a dimethylene unit by a *C,C*-triple bond leads to a strong increase of the $T_{N\text{-}I}$-values. Upon variation of the chain length R_1 (cf. esters *2–4*), alternation of both the melting and the clearing temperatures is observed. A noticeable feature is the relatively low melting point of *3*; this procures an attractive mesorange for this compound. Alternatively, if the chain length R_2 is varied (cf. esters *3*, *5* and *6*), a decrease in the melting and clearing points is noticed as the chain becomes longer; an optimum effect seems to be reached with $R_2 = CH_3$ (ester *3*).

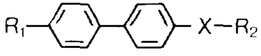
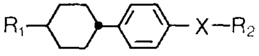
As expected, representatives of *p*-1-alkynylbenzoates (*7–9*) exhibit a lower tendency to form enantiotropic phases because of their greater ability to give rotation around the internal ester bond. Elongation of R_1 (*7–9*) leads to a continuous increase of the melting points and to alternation of the $T_{N\text{-}I}$-values, which, compared with the corresponding dimethylene analogs are still raised considerably.

As witnessed by the data for esters *10–12*, little or no improvement in the mesomorphic properties results from introduction of an acetylene unit into a terminal chain attached to a cyclohexyl ring.

Finally, the possibility of using the *C,C*-triple bond as a linking element in the core system exists. With regard to the transition temperatures of the corresponding hydrogenated ester, in the case of benzoate *13*, a marked increase in both T_m und T_c is apparent, whereas for the phenol ester *14*, this effect is less pronounced.

TABLE II

Comparison of the transition temperatures of acetylenic biphenyls and phenylcyclohexanes with those of their hydrogenated counterparts[a]

			X: C≡C					X: CH_2-CH_2				
Compound	R_1	R_2	No.	T_m	T_c	T_c-T_m	S/N	T_m	T_c	T_c-T_m	S/N	Lit./remarks
	C_5H_{11}	H	**15**	56,4	82,7	26,3	S	b	33,9		S	
	C_5H_{11}	CH_3	**16**	60,5	83,4	22,9	S	b	47,3		S	
	C_3H_7	H	**17**	38,9	[38,0]	−0,9		−1,5	[−75,0]	−73,5		7
	C_5H_{11}	H	**18**	39,4	42,1	2,7	N	5,5	[−35,0]	−40,5		
	C_7H_{15}	H	**19**	37,6	47,5	9,9	N	14,8	[−19,0]	−33,8		
	C_3H_7	CH_3	**20**	45,1	53,7	8,6	N	−11,5/ −4,1[c]	[−42,0]	−37,9		
	C_5H_{11}	CH_3	**21**	41,6	64,9	23,3	N	−9,3	(−11,9)	−2,6	N	
	C_7H_{15}	CH_3	**22**	43,5	66,8	23,3	N	−1,2/ 7,0[c]	7,7	0,7	S/N	$T_{S\text{-}N}$ = 6,5
	C_5H_{11}	C_2H_5	**23**	29,5	31,4	1,9	N					
	C_5H_{11}	C_3H_7	**24**	20,0	31,3	11,3	N	−0,8	(−5,0)	−4,2	S/N	8; $T_{S\text{-}N}$ = −8,0

---

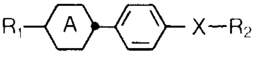
[a] *For the abbreviations used and additional remarks see Table I, footnotes a–c.*

[b] These compounds could not be crystallized even at low temperatures.

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

2. ACETYLENIC BIPHENYLS AND PHENYLCYCLOHEXANES (PCH)

This section covers compounds of the general structure I; the transition temperatures of which are summarized in Table II.



Ring *A* = phenyl, cyclohexyl

R_1, R_2 = H or alkyl

In contrast to the smectic biphenylacetylenes *15* and *16*, acetylenic representatives of the phenylcyclohexane series exhibit exclusively enantiotropic nematic behaviour. The T_c-values of the latter are increased by up to 110°C if compared with their hydrogenated counterparts (e.g. *17* or *20*). With regard to substitution at the *C*,*C*-triple bond, the propynyl chain clearly induces the highest clearing points (cf. *21* with *18*, *23* or *24*), an observation already made in the ester series. The influence of the length of the other chain R_1 on the $T_{N\text{-}I}$-values seems to be less pronounced (e.g. *20–22*), although we have only prepared odd-membered representatives.

In summary, liquid crystalline hydrocarbons have been found which exhibit attractive mesoranges.†

3. ACETYLENIC PHENYLCYCLOHEXYLETHANES (PECH)

Being aware of the often closely similar properties of phenylcyclohexylethanes (PECH) and phenylcyclohexanes (PCH), we have now prepared a number of representatives of the title compounds (Table III).

With regard to their phase transition temperatures, the following conclusions can be drawn:

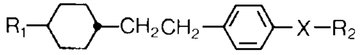
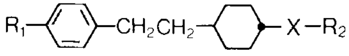
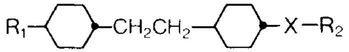
a. In comparison with the PCH-analogs (cf. Table II), the $T_{N\text{-}I}$-values of the new compounds are similar (cf. *26* with *18*, *27* with *19*,

---

† Additional physical properties of the new acetylenic liquid crystals will be discussed elsewhere.

TABLE III

Comparison of the transition temperatures of acetylenic phenylcyclohexylethanes with those of their hydrogenated counterparts[a]

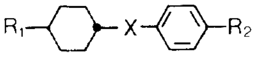
			X: C≡C					X: CH_2-CH_2				
Compound	R_1	R_2	No.	T_m	T_c	T_c-T_m	S/N	T_m	T_c	T_c-T_m	S/N	Lit./remarks
	C_4H_9	H	**25**	10,0	25,2	15,2	N					
	C_5H_{11}	H	**26**	25,5	42,5	17,0	N					
	C_7H_{15}	H	**27**	29,9	49,3	19,4	N	18,2	(13,1)	−5,1	N	
	C_4H_9	CH_3	**28**	33,1	38,6	5,5	N					
	C_5H_{11}	CH_3	**29**	46,8	55,3	8,5	N	4,5	18,0	13,5	S	9
	C_7H_{15}	CH_3	**30**	44,4	58,0	13,6	N	9,5	30,5	21,0	S	
	C_4H_9	C_2H_5	**31**	6,1	9,5	3,4	N					
	C_4H_9	C_3H_7	**32**	14,3	22,6	8,3	S					
	C_5H_{11}	C_3H_7	**33**	37,8	(30,9)	−6,9	S	9,7	30,4	20,7	S	9
	C_5H_{11}	H	**34**	34,8	—	—	—					
	OC_4H_9	H	**35**	39,5	—	—	—	4,0	6,5	2,5	S/N	9: $T_{S\text{-}N}=0$
	OC_4H_9	C_3H_7	**36**	21,6	25,3	3,7	S	25,5	45,0	19,5	S	9
	C_5H_{11}	H	**37**	51,2	68,0	16,8	N	2,5	76,0	73,5	S	

---

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

TABLE IV

Comparison of the transition temperatures of phenylcyclohexylacetylenes with those of their hydrogenated counterparts[a]

			X: $C \equiv C$					X: CH_2-CH_2				
Compounds	R_1	R_2	No.	T_m	T_c	T_c-T_m	S/N	T_m	T_c	T_c-T_m	S/N	Lit./remarks
	C_5H_{11}	H	**38**	17,1	—	—	—	−2,0	—	—		
	C_5H_{11}	CH_3	**39**	39,6	—	—	—					
	C_5H_{11}	C_5H_{11}	**40**	30,1	(25,0)	−5,1	N	9,5	30,0	20,5	S	9
	C_5H_{11}	OCH_3	**41**	30,9	45,7	14,8	N	31,0	33,0	2,0	N	9
	C_5H_{11}	OC_2H_5	**42**	70,4	75,3	4,9	N	18/27[b]	47,0	20,0	S/N	9; $T_{S\text{-}N} = 8,0$
	C_5H_{11}	OC_3H_7	**43**	65,1	(60,8)	−4,3	N	24,5	33,5	9,0	S/N	9; $T_{S\text{-}N} = 32,5$
	C_5H_{11}	OC_4H_9	**44**	44,3	70,0	25,7	N	25,5	45,0	19,5	S/N	9; $T_{S\text{-}N} = 44$

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

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

29 with *21*, *30* with *22* or *33* with *24*), the highest clearing points typically being induced by propynyl substituents.

b. In marked contrast to the PCH-analogs *17–19* are the lower melting points of the unsubstituted acetylenes *25–27*. As a consequence the latter exhibit a broader meso-range than the corresponding methyl-substituted representatives (cf. *25* with *28*, *26* with *29* and *27* with *30*).

c. The tendency to nematic behaviour is somewhat less pronounced than in the PCH-series; however, it is still more distinct than for the corresponding hydrogenated counterparts (e.g. *29*, *30*).

As in the ester series, a few representatives of cyclohexylacetylenes have been prepared for completeness. With the exception of the bicyclohexylacetylene *37*, which surprisingly exhibits purely nematic behaviour, these compounds do not seem to offer advantages over the hydrogenated analogs (e.g. *35* and *36*) with regard to transition temperatures.

4. PHENYLCYCLOHEXYLACETYLENES (PCA)

Although both polar and apolar tolanes have been known for a long time,[10] to our knowledge no members of the title class have been synthesized until now. The compounds prepared are presented in Table IV and compared with the corresponding dimethylene systems.

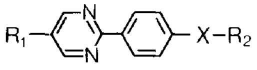
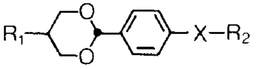
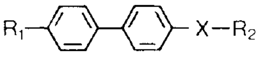
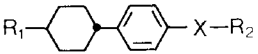
As can be seen from these data, dialkyl-substituted members of this family (*38–40*) have a considerably lower tendency to form mesophases than alkylalkoxy-substituted derivatives (*41–44*). However, the latter show high $T_{\text{N-I}}$-values and exclusively nematic behaviour. Since in comparison with the corresponding dimethylene compounds, both melting and clearing points are raised, the resulting meso-ranges are comparable.

5. APOLAR ACETYLENIC PYRIMIDINES AND DIOXANS

Since we have found earlier[1] that insertion of a *C*, *C*-triple bond into cyanopyrimidines and cyanodioxans leads to a marked increase in the T_c-values, we were interested to know if a similar effect arose for apolar members of these heterocyclic classes of mesogens. For this purpose, the compounds listed in Table V have been prepared and compared with their hydrogenated analogs or alternatively with the corresponding carbocyclic systems.

TABLE V

Comparison of the transition temperatures of acetylenic pyrimidines and dioxans with those of their carbocyclic analogs[a]

			X: C≡C					X: CH_2-CH_2				
Compound	R_1	R_2	No.	T_m	T_c	T_c-T_m	S/N	T_m	T_c	T_c-T_m	S/N	Lit.
	C_5H_{11}	H	**45**	72, 3	—	—	—					
	C_3H_7	CH_3	**46**	110, 5	[39, 0]	−71, 5		45, 3	[−17, 0]	−62, 3		
	C_4H_9	CH_3	**47**	69, 8	—	—	—					
	C_5H_{11}	CH_3	**48**	87, 8	[67, 0]	−21, 8						
	C_5H_{11}	H	**15**	56, 4	82, 7	26, 3	S	[b]	33, 9		S	
	C_5H_{11}	CH_3	**21**	41, 6	64, 9	23, 3	N	−9, 6	−11, 9	−2, 6		

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[a] For the abbreviations used and additional remarks see Table I, footnotes a–c.
[b] This compound could not be crystallized even at low temperatures.

None of these compounds showed either enantiotropic or monotropic mesomorphic behaviour. In the case of dioxan *48*, a virtual clearing point was determined and found to be in the same region as that of the PCH-system *21*. On the other hand, introduction of heteroatoms led to an increase in the melting points, an observation which was also made in the case of pyrimidineacetylene *45* (cf. with *15*).

CONCLUSIONS

Replacement of a dimethylene unit by a *C*, *C*-triple bond at different positions in well-established apolar LC-materials leads to new liquid crystals with mesophases of generally higher thermal stability. The degree of increase in the $T_{N\text{-}I}$-values seems to depend on the location of the ethynylene unit. Thus, whereas phenylacetylenes exhibit clearing temperatures raised by up to 100°C, cyclohexylacetylenes differ little from their hydrogenated analogs.

Throughout all classes investigated, a strong tendency to formation of *nematic* mesophases was noticed.

EXPERIMENTAL

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

Acknowledgements

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