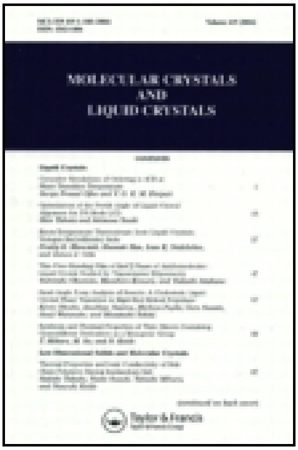

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Synthesis, Mesomorphic Properties and Chemical Stability of Some Fluoro Terminally Substituted Acetylenes

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Synthesis, Mesomorphic Properties and Chemical Stability of Some Fluoro Terminally Substituted Acetylenes

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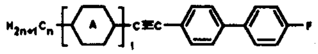
Preparative methods and thermal stability of disubstituted LC acetylenes with a -C≡C- or -CH_2CH_2-C≡C- bridge between cyclohexyl and fluorobiphenyl moieties are described. The degradation products resulting from heating at 150°C in air or a vacuum were analyzed.

Keywords: synthesis of liquid crystals; fluoroacetylene compounds; thermal stability

INTRODUCTION

The fluorinated LC compounds attract a great attention, because of their high chemical stability and electrical resistivity. Their holding ratio is high and their viscosity low. The dielectric and optical anisotropy is modest[1+3]. The introduction of an acetylene bond into a molecule causes the increase of the LC material birefringence which is useful for some applications. However, it was found that acetylenes with fluoro terminal group such as tolanes containing no other than aromatic rings have high melting points[4,5], what limits their contents in liquid crystal mixtures. When an aromatic ring is replaced by cyclohexane one the depression of melting points is observed. Some of these compounds have already been prepared[6+10] but their chemical stability has not been investigated. The most interesting structures seem to be those with a cyclohexane ring attached directly to the triple -C≡C- bond. Schadt and Villiger obtained these compounds starting from 4-substituted cyclohexyl acetylenes[6,10]. The aim of this paper is to show a simpler and more general method as well as to test the thermal stability of the produced compounds.

The compounds of general formula 1



1

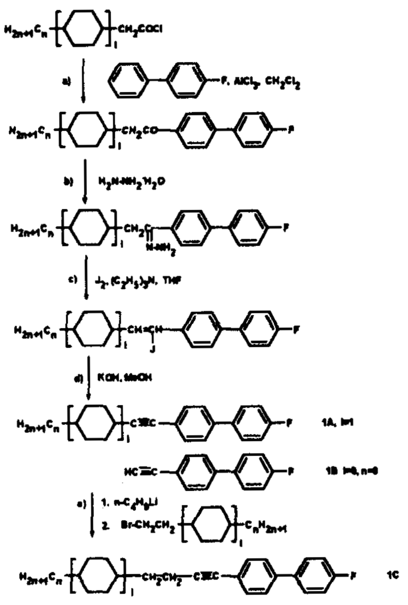
A = cyclohexyl ring or cyclohexylethyl group

have been synthesized and their thermal stability has been compared with the stability of previously prepared similar compounds.

SYNTHESIS

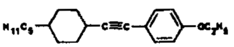
Compounds 1 were prepared according to the method outlined in scheme 1.

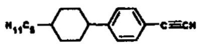
4-Fluorobiphenyl was acylated, in a known way, with trans-4-alkylcyclohexylacetyl chloride [9] in the case of 1A or acetyl chloride in the case of 1B. The ketone obtained in step (a) was treated with hydrazine hydrate and the resulting hydrazide was transformed into iodoethene derivative under the action of iodine in the presence of triethylamine (step c). Then it was boiled with KOH in methanol to eliminate HI. 1-(trans-4-alkylcyclohexyl)-2-(4'-fluorobiphenyl-4-yl)acetylene (compound 1A) or 4-ethynyl-4'-fluorobiphenyl (compound 1B) were formed with a good purity and yield.



SCHEME 1 Route of preparation of 1-alkylcyclohexyl-2-(4-fluorobiphenyl-4-yl)acetylenes (1A) and 1-(trans-4-alkylcyclohexylethyl-2-)-2-(4'-fluorobiphenyl-4-yl)acetylenes (1C).

Compound 1B was treated with butyllithium and then with 1-(trans-4-cyclohexyl)-2-bromoethane as we previously described in Ref.[9] and 1-(trans-4-alkylcyclohexylethyl-2)-2-(4'-fluorobiphenyl-4-yl)acetylene (compound 1C) was produced. The method shown in scheme 1 was also used with good results for the preparation of compounds 1D and 1E


1D


1E

The method presented above seems to be very convenient for preparing, in laboratory scale, different acetylene derivatives especially with the acetylene unit between the cyclohexane and benzene rings.

MESOMORPHIC PROPERTIES

Like 4-pentyl-4'-fluorotolane the isomeric 4-pentylethynyl-4'-fluorobiphenyl (compound 1A1) is not mesomorphic, see Table I.

TABLE I Comparison of phase transition of monofluoroterminally substituted acetylenes; temperatures are given in °C, enthalpies in kcal/mol

No	R	Cr_1		Cr		S_B		S_A		N		I	Ref
				$R-C\equiv C-C_6H_4-C_6H_4-F$									
1A1	$H_{11}C_5$			•	56.5	-		-		-		•	x
1A2	$H_7C_3-C_6H_{10}-$			•	110.6	-		-		•	179	•	6
1A3	$H_9C_4-C_6H_{10}-$			•	88.7	-		-		•	94.1	•	6
1A4	$H_{11}C_5-C_6H_{10}-$			•	89.7			•	93.7	•	168.2[a]	•	x
					5.2				0		0.32		
1C1	$H_7C_3-C_6H_{10}-CH_2CH_2$			•	88.2	•	(62.5)	-		•	106.6[a]	•	x
1C2	$H_{11}C_5-C_6H_{10}-CH_2CH_2$	•	58.0	•	83.0	•	(59.2)	-		•	107.8	•	x
			2.47		4.48								
2	$H_{11}C_5-C_6H_4-$	•	104.4	•	161.8	•	170.9	-		•	210	•	x
			2.96		0.16		3.0						
				•	165	-		-		•	205	•	5
				$R-C\equiv C-CH_2CH_2-C_6H_{10}-C_6H_4-F$									
3	$H_{11}C_5-C_6H_4-$			•	62.7	-		-		•	57.2	•	9
					5.72						0.86		
4	$H_{11}C_5O-C_6H_4-$			•	69.0	-		-		•	84.2	•	
5	$H_{11}C_5-C_6H_{10}-C_6H_4$			•	126.6	•	(84.3)	•	(104)**	•	171	•	x
					7.9				0.19		1.0		
				$R-C_6H_4-C\equiv C-C_6H_4-F$									
6	$H_{11}C_5-$	•	6.12	•	64.2	-		-		-		•	4
7	$H_{11}C_5O-$			•	57.7	-		-		-		•	4
8	$H_7C_3-C_6H_{10}-$			•	94	-		-		•	192	•	8
9	$H_7C_3-C_6H_{10}-CH_2CH_2$			•	86	-		-		•	149	•	7

x - prepared in this work, ** - S_C phase

a - for comparison $H_{11}C_5-C_6H_{10}-C_6H_4-C_6H_4-F$ - Cr 100 N 153 I[12] and $H_{11}C_5-C_6H_{10}-CH_2CH_2-C_6H_4-C_6H_4-F$ - Cr 82 N 121 I[13].

Compound 1A1 prepared by treating 1B with BuLi and then with $H_{11}C_5Br$; Compound 2 prepared by treating 1B with $H_{11}C_5-C_6H_4-I$ in the presence of $PdCl_2[Ph_3P]_2$, CuI; Compound 5 prepared by treating 1E with BuLi and then with 2-bromo-1-(trans-4-(4-fluorophenyl)cyclohexyl.

Three-ring 1-(trans-4-alkylcyclohexyl)-2-(4'-fluorobiphenyl-4-yl)acetylenes (compounds 1A2-4) with a short alkyl are nematics and with a longer alkyl n=5 show a nematic and smectic A phases. Three-ring 1-(trans-4-alkylcyclohexylethyl-2)-2-(4'-fluorobiphenyl-4-yl)acetylenes (compounds 1C1-2) are nematics with a monotropic B phase. Their clearing points are lower, but higher than observed for isomeric compound 3. Four-ring compound 5 shows a monotropic smectic B and a smectic C phase, but its melting point and melting enthalpy are very high and therefore its solubility in LC mixtures is very poor. The order of the clearing points of the pentyl derivatives of the monofluoro terminally substituted three ring acetylenes is the following:

2>1A4>1C2>3.

Similar correlation was found in analogues fluorohydrocarbons without -C≡C- bridge. The introduction of the $-CH_2CH_2-$ bridge between rings depresses the clearing point, although less than it is observed in the case of simultaneous presence of the $-CH_2CH_2-$ and -C≡C- bridge. The order of the clearing points correlates mainly with a sequence rings in the rigid core. The presence of the -C≡C- bridge modifies only the observed correlation. The introduction of the -C≡C- bridge between the cyclohexane and biphenyl rings increases the clearing temperature by about 25 deg and slightly decreases the melting point (10 deg). The introduction of the flexible $-CH_2CH_2-$ bridge decreases the melting points by about 20 deg and clearing points by 30°C[11,12] but at the same time the introduction of the $-CH_2CH_2-$ and -C≡C- bridge results in further decrease of the clearing points and the B phase appears as monotropic one. For this reason the $-CH_2CH_2-$C≡C- group is not a convenient bridging group for LC structures. This group depresses stronger the clearing point of structure 3 than of 1C2. The depression adds to the depression originating from the position of the cyclohexane ring in the central part of molecule.

The models of molecules in their most thermodynamically stable forms are compared below:

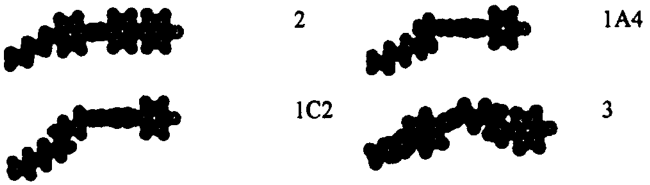
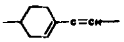


FIGURE 1 Molecular configuration calculated by "HyperChem".

The molecular configuration calculated using „HyperChem" correlates very well with the observed mesomorphic properties. The molecule of compound 2 is linear and resembles a cylinder. The molecule 1A4 is bent; the rigid cyclohexane ring can not follow the geometry of the ethynyl biphenyl moiety. The introduction of the flexible -CH_2CH_2- group between a cyclohexane ring and the -C≡C- bridge increases the bent part of the molecule 1C2 and 3. This shape is responsible for the great increase of viscosity observed for 3[9].

THERMAL STABILITY

Thermal stability was tested as follow: the samples of the compounds (0.20 g of pentyl derivatives) were heated at 150°C in an open ampoule for 2 and 5 hours or in a sealed evacuated ampoule for 5 hour. Then the samples were dissolved in $CHCl_3$ (compound 2 was dissolved in THF) and analyzed using a gas chromatograph Hewlett-Packard series HP5890. The flame ionization detector (FID), mass detector HP 5972, capillary columns HP1 and HP5 and split-splittless injector were used. The injector temperature was 300°C. The compound 1A1 not investigated, because it was unstable. When it was kept at room temperature in a transparent bottle it quickly turned yellow. The initial purity the of other tested compounds was in the region of from 97.7 % (for 2) to 99.7 (for 1D), Table II. Most of them contained only three significant impurities. One of them was the butyl member of the same homologous series. Compound 3 and 5 with the -C≡C-CH_2CH_2- bridge (but not 1C2) contained more trace impurities and two of them were more volatile, probably they appear during the decomposition in the chromatographic injector. In the case of „fully" aromatic compound 2 the other impurities had the same molecular weight as compound 2 but their alkyl chain is branched (1-methylbuthyl or 2-methylbuthyl). The cis isomer was the main impurity of the compound with a cyclohexane ring 1A4, 1C2, 3, 5 and 1D. The compounds 1A4 and 1D contained also small amounts of conjugated cyclohexylene derivatives with moieties such as: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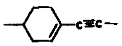
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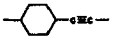

Compound 1C2, 3 and 5 contained impurities with the other conjugated bridges: -C≡C-CH=CH- and -CH=CH-C=CH- instead of -C≡C-CH_2CH_2-.

The compound heated in a vacuum at 150° decomposed slowly:

$$2 \sim 1D \sim 1A4 \sim 5 < 3,$$

see data in Table II.

The contents of the impurities is less than one percent after 5 hours; compound 3 decomposed faster and a diversity of degradation products appeared; most of them had lower molecular weight. The presence of air strongly accelerates the decomposition and increases the number of products (especially with low molecular weights).

TABLE II The comparison of purity (%)* of compounds before the stability test (column a) and the contents (%) of the compounds after heating for 2 hours at 150° (column b) or 5 hours at 150° (column c) or 5 hours at 150° in a sealed evacuated ampoule - upper line, number of impurities - lower line (first column - degradation products with much lower molecular weights, second column - impurities with similar or higher molecular weights

compound	a	b	c	d
2	97.70	81.70	70.21	96.92
	- 3	3 5	4 9	1 6
1A4	99.13	87.61	82.86	97.20
	- 3	3 11	3 11	1 9
1C2	99.06	94.79	91.69	
	3 2	6 2	6 2	
3	99.48	71.22	54.35	91.21
	2 7	6 19	6 19	6 15
5	98.62	91.44	79.14	98.20
	2 12	2 22	2 22	1 11
1D	99.66	89.74	75.57	98.26
	- 3	1 6	1 6	- 7

* - calculated from the area of a chromatographic peak

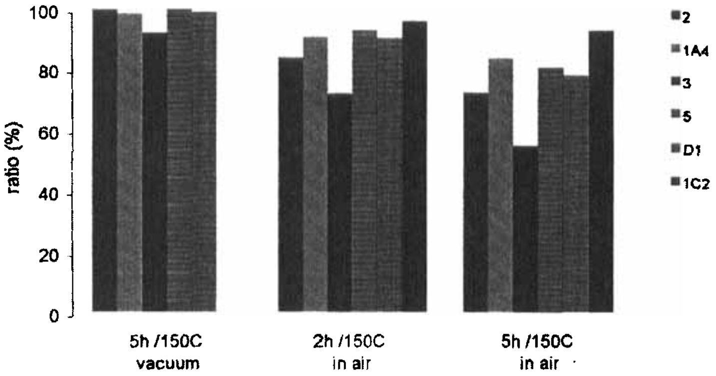

FIGURE 2 Ratio (%) of concentration of the investigated compounds in a sample after and before the test.

The same number of products was found after 2 hours and after 5 hours of heating; the difference was only in their quantity. In Fig. 2 the decrease of the content of the starting materials in samples are compared; their stability changes as follow:

$$1C2 \approx 1A4 > 5 > 1D > 2 > 3$$

The content of the most stable compounds 1C2 and 1A4 decrease by about 7÷16 % and the content of the least stable 3 by about 43 %. It is interesting that „fully" aromatic compound 2 (the -C≡C- bridge between benzene rings) decomposes more quickly than compound 1A4 containing the -C≡C- bridge between cyclohexane and benzene rings. The big difference in the stability of the compounds 3 and 1C2 is surprising. Table III shows main decomposition products in the samples heated at 150° for 5 hours. The low molecular decomposition products are mainly ketones, alcohols and aldehydes.

TABLE III The main low (column a) and high (column b) molecular weight products appearing after heating for 5 hours in air at 150°

	a	b
1D	4-pentylcyclohexanone	$H_{11}C_5$-$C_6H_9OH^*$-$C\equiv C$-$C_6H_4OC_2H_5$, $H_{11}C_5$-$C_6H_{10}CH_2CO$-$C_6H_4OC_2H_5$
1A4	4-pentylcyclohexanone	$H_{11}C_5$-$C_6H_9OH^*$-$C\equiv C$-C_6H_4-C_6H_4-F
	4'-fluorobiphenyl-4-aldehyde	
	4'-fluorobiphenyl-4-carboxylic acid	$H_{11}C_5$-$C_6H_{10}CH_2CO$-C_6H_4-C_6H_4-F
1C2	The same as 1A4 and 4-pentylcyclohexenone	
3	$HOCH_2$-C_6H_{10}-C_6H_4-F	
	$HOCH_2$-CH_2-C_6H_{10}-C_6H_4-F	$H_{11}C_5$-C_6H_4-CH=CH-CH_2-CH_2-C_6H_{10}-C_6H_4-F
	OCH-C_6H_4-C_6H_4-F	
	$OCHCH_2$-C_6H_4-C_6H_4-F	
5	The same as 3 and $H_{11}C_5$-C_6H_{10}-C_6H_4-CHO	
2	4'-fluorobiphenyl-4-aldehyde	H_9C_4-CO-C_6H_4-$C\equiv C$-C_6H_4-C_6H_4-F, H_7C_3CH=CH-C_6H_4-$C\equiv C$-C_6H_4-C_6H_4-F, $HOCH_2C_6H_4$-$C\equiv C$-C_6H_4-C_6H_4-F,

* - hydroxyl in position 1.

CONCLUSION

The Japanese industry proposed to heat LC compounds at 150° in air during 1 hour to test their thermal stability. Our results show that very deep transformations of the compounds occur at this conditions. The compounds are oxidized and hydrated and the previously formed products decompose yielding compounds with smaller molecular weights. Thermal stability test at 150° in air may be useful to compare of stability of different compounds among themselves, but the results can not be extrapolated to the behavior of LC at lower temperatures in which they are usually being used. The stability of monofluorobiphenyl ethynyl benzenes and cyclohexanes is comparable with the stability of the 4-(trans-4-cyclohexyl)fluorobenzene, which after heating for 5 h at 150°C in air decomposed in 5%[13]. The „fully" aromatic compound 2 is oxygenated mainly at the alkyl chain in α position to the benzene ring. The compound 1D and 1A4 are oxygenated mainly at the secondary atoms of the cyclohexane ring. Some compounds with the -C≡CCH$_2$CH$_2$- bridge are not stable, they are easy oxygenated at -CH$_2$CH$_2$- group and many low-molecular-weight products are formed.

Acknowledgments

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