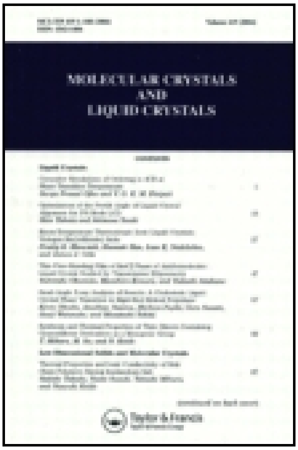

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Synthesis and Mesogenic Properties of 1-Phenyl-4-(4-*n*-Alkoxyphenyl-2,3,5,6-Tetrafluorophenyl)-Butadiynes

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Three series of 1,4-disubstituted butadiynes containing a tetrafluorophenylene in core structure have been synthesized from 1-pentafluorophenyl-2-trimethylsilyacetylene. The results showed that 1-phenyl-4-(4-*n*-alkoxyphenyl-2,3,5,6-tetrafluorophenyl)-butadiynes were nematic liquid crystals. However, 1-phenyl-4-(4-*n*-alkoxy-2,3,5,6-tetrafluoro-phenyl)-butadiynes and 1-(4-nitrophenyl)-4-(4-*n*-alkoxy-2,3,5,6-tetrafluorophyenyl)-butadiynes did not exhibit any liquid crystallinity. The IR spectra showed that the 1-phenyl-4-(4-*n*-alkoxyphenyl-2,3,5,6-tetrafluorophenyl)-butadiynes were good liquid crystals for IR modulator.

Keywords: Butadiynes; mesomorphism; tetrafluorophenylene; fluorinated LCs

1. INTRODUCTION

The disubstituted butadiyne LCs were first synthesized by Grant [1]. From then on, the work on butadiyne LCs has been continuously active. A variety of properties of butadiyne LCs, including physical properties, non-linear optical properties and polymerization behavior were investigated extensively [2–5]. The butadiyne LC compounds are expected to be very useful liquid crystal candidates for IR modulators where photostability is not a problem [6, 7].

Asymmetric 1,4-disubstituted butadiyne LCs are found to possess a high birefringence, low viscosity and reasonably high dielectric anisotropy [2, 6].

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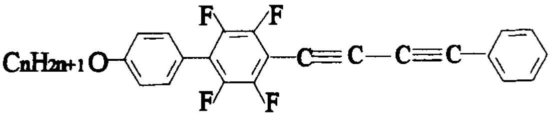
Those properties fit the requirements for modulators rather well. LCs are often modified via substitution of hydrogen(s) by fluorine(s) in core structure [8, 9]. The introduction of fluorine to LC molecules can usually lower the melting point and viscosity resulting from relatively small intermolecular interaction of fluorinated compounds and destruction of molecular symmetry. The presence of mono- or di- fluorine in LC core structure lowers the melting points and widens the mesophase ranges [10, 11]. However, there are rarely such studies on butadiyne LCs [2] and no report on polyfluoro-substituted butadiyne LCs. Therefore, the main objective of this work is the synthesis of such LCs and observation of their mesomorphism.

Several series of 1,2-substituted acetylene LCs have been synthesized in our group [12, 13], but nothing has been done on remarkable butadiyne mesogens. This paper presents a series of 1,4-disubstituted butadiyne LCs containing a tetrafluoro-substituted phenylene in core structure (1),



(1)

(1a)n=4, (1b)n=5, (1c)n=6, (1d)n=7, (1e)n=8, (1f)n=9, (1g)n=10.

whose mesomorphism was investigated for a better understanding of the relationship between phase transition and terminal alkoxy length.

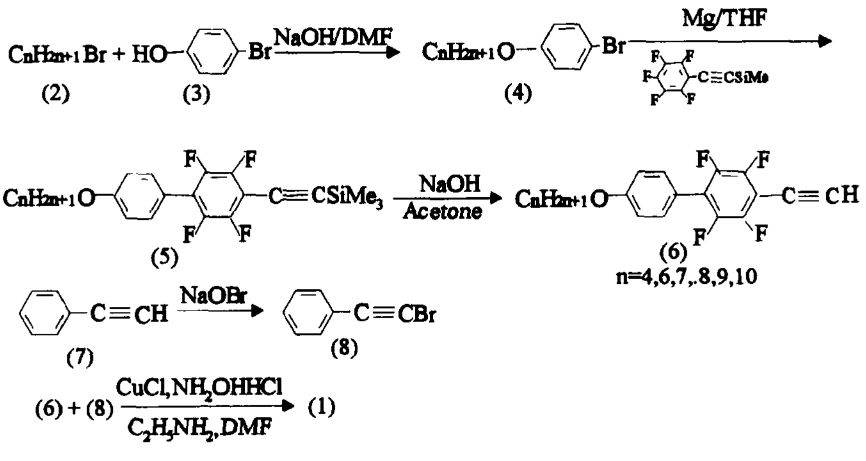
2. INSTRUMENTATION

The infrared spectra were determined with a Bio-Rad Digilab FTS-20E. The ^1H NMR spectra were recorded on a Varian EM 360 L (60 MHz) or FX-90Q (90 MHz) spectrometer with TMS as internal standard, and ^{19}F NMR spectra were recorded on Varian EM 360L spectrometer with trifluoroacetic acid as external standard. Mass spectra were measured with a Finnigan 4021 spectrometer. Elemental analysis used a Mod. 1106 spectrometer (Carlo Erba Strumentazione, Italy) to determine the contents of C and H. The mesophase textures were observed using a Mettler FP-52 heatstage with a FP-5 control unit in conjunction with an Olympus BH2 polarizing microscope. The transition behaviors were confirmed by a differential scanning calorimeter on a Shimadzu DSC-50 system and data station and the transition peaks were used as the transition temperatures.

3. SYNTHESIS

The liquid crystal molecules studied were synthesized following the route as shown in Scheme 1. The intermediates (4), *p*-*n*-alkoxyphenyl bromides, were prepared readily from alkyl bromides and *p*-bromophenol by Williamson reaction [14]. Compounds (4) reacted with 1-pentfluorophenyl-2-trimethylsilylacetylene to afford the compounds (5), which was removed of the trimethylsilyl protecting group in basic solution to give 4-(4-alkoxyphenyl)-2,3,5,6-tetrafluorophenylacetylenes (6) [15].

The target LC molecules (1a) to (1g) were obtained by the Chodkiewicz-Cadiot coupling [16] of compounds (6) and 1-phenyl-2-bromoacetylene (8) which was prepared via bromination of phenylacetylene (7) with sodium hypobromide [17].



Scheme 1

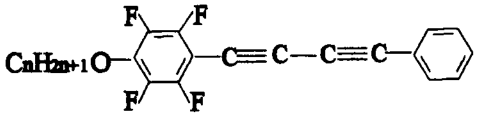
The synthesis of compounds (5) and (8) were reported elsewhere [12, 17]. As an example, the synthesis of compound (1a) is described below.

(1a) 1-phenyl-4-(4-*n*-butyloxyphenyl-2,3,5,6-tetrafluorophenyl)-butadiyne

To an *N*,*N*-dimethylformamide (2ml) solution of 140 mg (0.46 mmol) 4-(4-*n*-butyloxyphenyl)-2,3,5,6-tetrafluorophenylacetylene (6a) containing 0.3 ml of ethanolic solution of ethylamine (70%) and catalytic quantity of cuprous chloride (2 mg), hydroxylamine hydrochloride (5 mg) was added. After a while, a little acetylene copper (I) emerged, then 1-phenyl-2-bromoacetylene (0.3 ml, 2.6 mmol) in 0.5 ml of *N*,*N*-dimethylformamide was dropped into the above solution for 0.5 h. The mixture was stirred for about 2 hrs and any blue color which developed was discharged by addition of further small quantities of NH_2OHHCl and $C_2H_5NH_2$ during the reaction. The mixture, which finally turned brown, was acidified with 0.5N HCl, and 30 ml of H_2O was added. The products were extracted with ether three times. The extracts were combined, washed with water, dried over $MgSO_4$ and evaporated to dryness. The residues were purified by column chromatography on silica gel using petroleum ether as eluent to give light yellow crystals, which were recrystallized from ethanol to give white crystals. Yield 130 mg (67.0%). M.P. 113.1°C. IR. (cm^{-1}) 976.4, 1184.1, 1254.5, 1474.9, 2223.8, 2956.1. ^1H NMR(60 MHz, CCl_4/ TMS) δ:0.90 (t, 3H, J = 5.6 Hz, CH_3), 1.12–1.81 (m, 4H), 3.84(t, 2H, J = 6.0 Hz, OCH_2), 6.98(d, 2H, H_{arom} ortho to C_4H_9O), 7.10–7.43(m, 7H, H_{arom}). ^{19}F NMR, δ:59.3(m, 2F, F_{arom}), 67.3(m, 2F, F_{arom}). MS m/z: 422(m^+), 423, 366, 367. Analysis(%): Found C74.27, H4.15. F17.84, Calc. for $C_{26}H_{18}F_4O$, C73.93, H4.29, F17.99.

All of the intermediates and new compounds have satisfactory elemental analysis results and appropriate IR, MS, ^1H and ^{19}F NMR spectra data.

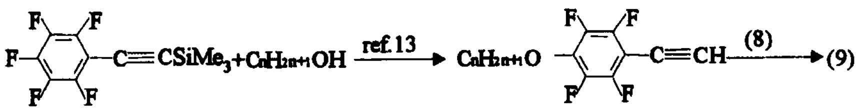
A series of 1-phenyl-4-(4-*n*-alkoxyphenyl-2,3,5,6-tetrafluorophenyl)-butadiynes as the following structure (9),



(9)

(9a)n=6; (9b)n=7; (9c)n=8

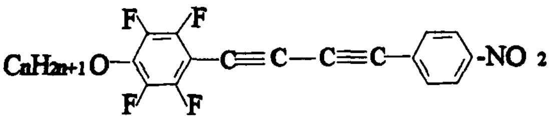
were synthesized. The proceed are given in Scheme 2.



Scheme 2

4. RESULTS AND DISCUSSION

Wu and co-workers [6, 7] reported that butadiynes with asymmetric tails offer compounds with low melting points and broad nematic ranges. We wish to synthesize diphenyl-substituted butadiynes which have only one tail as the structure (9) which contains a 2,3,5,6-tetrafluorophenylene in the core part. Unfortunately, the compounds (9a), (9b) and (9c) do not have liquid crystallinity. It is probably due to the bulky tetrafluorophenylene instead of phenylene, the terminal phenyl without a polar group, or the combination of the two. Wu and co-workers have synthesized 1-(4-chloro (or cyano)-phenyl)-4-(4′-alkylphenyl)-butadiynes [6, 7]. The 1-(4-chloro-phenyl)-4-(4′-alkylphenyl)-butadiynes with ethyl, butyl and hexyl as alkyl tails do not exhibit the mesophase at all. The 1-(4-cyanophenyl)-4-(4′-hexyl (or octyl)-phenyl)-butadiynes exhibit a monotropic nematic phase. But their nematic ranges are only about 2 degrees. These results show that the large polarity of the polar group attaching to the rod-like molecular terminal was likely to enhance the mesogenic property. We probably can obtain LCs if a polar group, such as NO_2, halogen or CN, substitutes the para-H of terminal phenyl of compounds (9). Herein, the 1-(4-nitrophenyl)-4-(4-alkoxy-2,3,5,6-tetrafluorophenyl) butadiynes(10) were synthesized



(10)

(10a)n=7, (10b)n=8, (10c)n=9

Unfortunately again, the butadiynes (10) also do not show liquid crystallinity and their melting points are as high as 170° C. At this temperature the substances polymerize.

The presence of a polar group raises the melting point considerably, but a high melting point must be avoided in practical use. Because of this, we try to avoid introducing the polar group, and alternatively to extend the length of the rigid core structure of the molecule to improve liquid crystallinity and wished to keep the melting point at a relatively low temperature. Thus, we inserted a phenylene in the compounds (9) resulting in the structure like compounds (1).

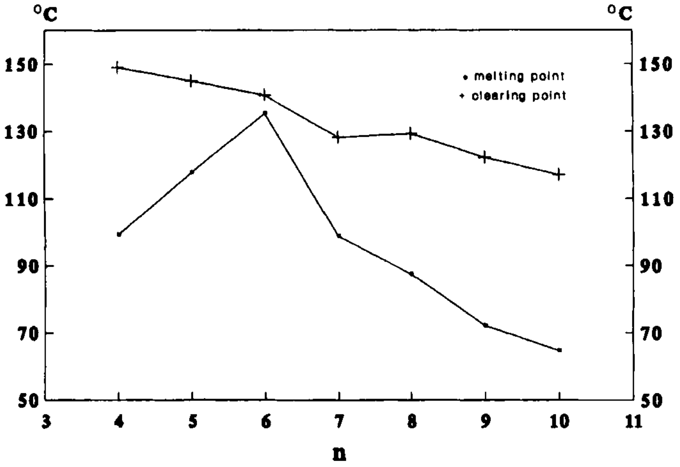


FIGURE 1 The methylene number(n) Vs. M.P. and C.P.

Seven new fluorinated compounds (1a) to (1g) obtained exhibit liquid crystallinity. The transition temperatures of a cycle of heating and cooling are presented in Table I. For clear comparison, the plots of the melting points and clearing points against the methylene number of alkoxy are given in Figure 1. The melting point reaches a maximum at $n = 6$. However, the clearing points fall with the increase of the tail chain length, resulting in the fact that the compound (1c) has the narrowest nematic range among them. The mesogen (1g) has the widest nematic range from 64.7 to 117.1°C. The fact that the melting point of the mesogen (1c) is much higher than that of the mesogen (1a) and (1b) needs further study. At present, we attribute this divergence to the absence of a polar group on one end of the molecule, which causes the decrease of terminal intermolecular cohesion, and attribute to the more obvious effect of the length of tail chains on the whole molecular polarization. However, it could be concluded that the melting points reduce with the growing terminal alkoxys, as regular LC homologues do.

The high members of the homologues do not exhibit smectic phase, probably because of the bulky tetrafluorophenylne in the core structure resulting in greater separation of the aromatic nuclei and the decrease of the lateral intermolecular attraction.

The compounds (1e), (1f) and (1g) exhibit relatively low absorption between 1600 to 4000 cm^{-1} on IR spectra, as shown in Figure 2. So, these LCs may find applications in IR modulators.

TABLE I Phase transition temperature(° C) of the compounds (1)

No.	*n*	*Phase transition temperatures/° C* *
1a	4	$C \underset{99.3}{\overset{135.7}{\rightleftharpoons}} N \underset{149.1}{\overset{149.5}{\rightleftharpoons}} I$
1b	5	$C \underset{117.8}{\overset{125.0}{\rightleftharpoons}} N \underset{145.0}{\overset{145.5}{\rightleftharpoons}} I$
1c	6	$C \underset{135.4}{\overset{137.0}{\rightleftharpoons}} N \underset{140.8}{\overset{140.8}{\rightleftharpoons}} I$
1d	7	$C \underset{98.9}{\overset{102.2}{\rightleftharpoons}} N \underset{128.3}{\overset{128.0}{\rightleftharpoons}} I$
1e	8	$C \underset{87.5}{\overset{100.9}{\rightleftharpoons}} N \underset{129.4}{\overset{129.5}{\rightleftharpoons}} I$
1f	9	$C \underset{72.2}{\overset{84.4}{\rightleftharpoons}} N \underset{122.3}{\overset{122.4}{\rightleftharpoons}} I$
1g	10	$C \underset{64.7}{\overset{68.1}{\rightleftharpoons}} N \underset{117.1}{\overset{118.2}{\rightleftharpoons}} I$

*C, crystal; N, namestic; I, isotropic.

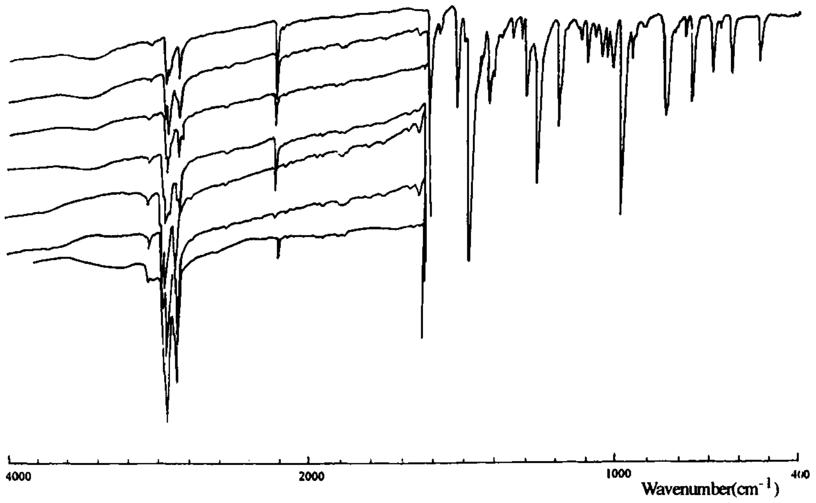


FIGURE 2 The IR of compounds (1). The whole range IR of the compound (1a) is given only, the (1b) to (1g) have similar corresponding absorption between 400 and 1600 cm^{-1}.

However, the melting points of compounds (1) are a little high because of the rigid structure of biphenylene and the large π conjugation. Thus, the one-tail butadiyne mesogens (1), especially (1f) and (1g), are expected to be good host candidates for forming a eutectic mixture with a wide nematic range.

Acknowledgements

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