Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Chizu Sekine, Koichi Fujisawa, Yukari Fujimoto & Masayoshi Minai (1999): Optical Anisotropy of Phenylacetylene Homologues, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 235-242

To link to this article: http://dx.doi.org/10.1080/10587259908023765

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 235-242
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Optical Anisotropy of Phenylacetylene Homologues

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In order to study the relationship between the chemical structures and the optical anisotropic properties of liquid crystalline materials, we synthesized and evaluated phenylacetylene homologoues. The mesomorphic properties and birefringence of the compounds will be presented. The relationship between the calculated anisotropy of polarizability ($\Delta\ \alpha$) and observed optical anisotropy was also investigated. Δ n increased with calculated $\Delta\ \alpha$, but some compounds having substituent groups and 1-ring compounds exhibited lower Δ n than some compounds which have almost same $\Delta\ \alpha$.

Keywords: Optical Anisotropy; Anisotropy Of Polarizability; Birefringence; Phenylacetylene

INTRODUCTION

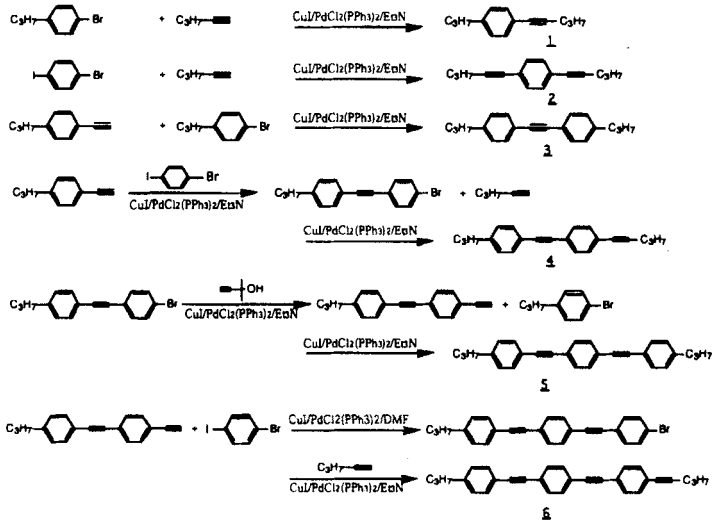
Liquid crystals with high birifringence (Δn) are useful components of liquid crystal mixtures. They are indispensable materials for widely employed super twisted nematic(STN) devices. Besides these conventional display devices, they are also applicable for PDLC and spatial light modulators[1],[2],[3],[4]. For these purposes, a number of high Δn liquid crystals have been investigated[5],[6],[7].

It is well known that high Δn can be achieved by increasing the molecular conjugation length[2]. We synthesized and evaluated phenylacetylene homologues as a highly conjugated molecules along the molecular long axis. We studied the influences of core structures and substituent groups on physical properties.

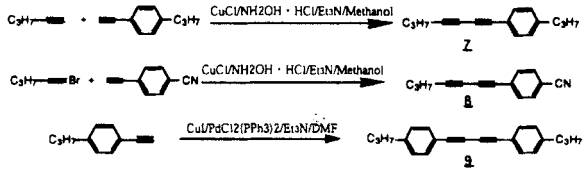
EXPERIMENTALS

SYNTHESIS

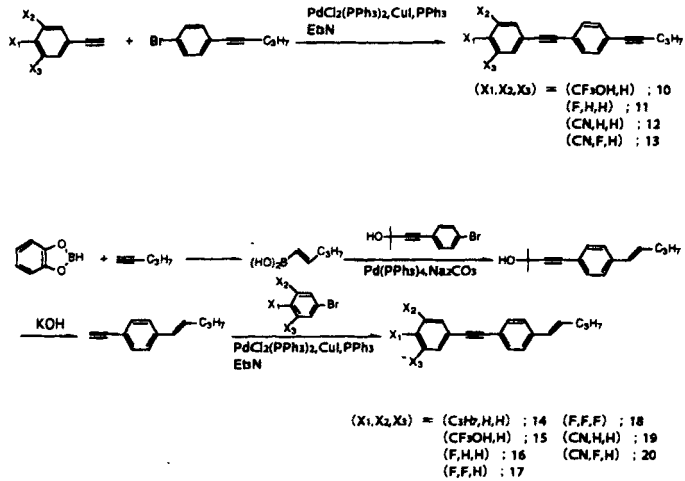
The synthesis routes of phenylacetylene derivatives are shown in SCHEME 1,2 and 3. Compound**1**～**9** were synthesized by coupling of bromided intermediates and ethynyl intermediates. Alkenyl type (**14**～**20**) were synthesized by the palladium-catalyzed coupling reaction of alkenylboronic acids with arylbromides.



SCHEME1 Syntheses of phenylacetylene series



SCHEME2 Syntheses of phenylacetylene series(diacetylene type)



SCHEME3 Synthesis of substituted alkynyltolane and alkenyltolane derivatives

The structures of final compounds and various synthetic intermediates were charactarized by 1-H-NMR spectroscopy. All spectra were recorded in $CDCl_3$ with TMS as internal standard. The purity of each compound was checked by HPLC analysis (ODS A-212 column,Sumika Chemical Analysis Service) and all compounds were 99> percent pure.

MEASUREMENT

Transition temperatures and phase sequences were measured using a Mettler FP82 hotstage and control unit in conjunction with optical microscopy (OPTIPHOT2-POL,Nikon) and these were comfirmed using differential scanning calorimetry using a DSC-200 (Seiko Instruments Inc.).

Birefringence values were measured as extrapolated values from mixtures which are 10 percent w/w solution of each test compound in MJ931381(Merck Japan). Abbe refractometer (2T, ATAGO) was used to measure the refractive indices of the mixtures at 20℃. A sodium lamp was used to provide the light

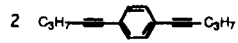
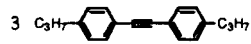
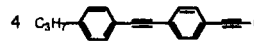
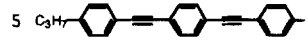
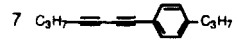
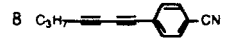
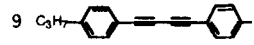
source at 589nm.

RESULTS AND DISCUSSIONS

Influences of core structures on physical properties

The phase sequences and transition temperatures of compounds1～9 are shown in TABLE1. The melting points of these compounds and nematic tendencies increased with the increase in the number of phenylacetylene unit. 1 and 2-ring compounds did not exhibited liquid crystal phases, but 3-ring compounds showed enantiotropic liquid crystal phases. Δn also increased in keeping with the unit number as expected. Diacetylene types showed higher melting points and larger Δn compared with phenylacetylene types in which the number of

Table1 Physical proprties of phenylacetylene derivatives

		Phase sequences /℃	Δ n[1)]
1		(-50<)I	0.0
2		K(47.0)I	0.115
3		K(72.5)I	0.264
4		K(98.8)I	0.351
5		K(169.7)Sx(178.3)N(244.5)I	0.496[2)]
6		K(193.5)N(264.6)I	—[3)]
7		K(7.1)I	0.183
8		K(98.7)I	0.335
9		K(107.9)N(132.7)I	0.410

1)Extrapolated values from liquid crystal (10wt%) mixed in nematic host MJ931381 (at 20℃ and 589nm)
2)Extrapolated values from liquid crystal (5wt%) mixed in nematic host MJ931381
3)Insoluble in MJ931381

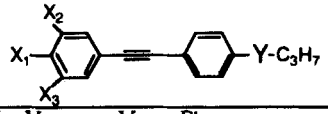
phenyl rings and etynyl groups are the same. 3-ring compounds exhibited broad nematic phase and large Δn.

Influences of substitution on physical properties

The phase sequences and transition temperatures of substituted alkynyltolane (compound4,10~13) and alkenyltolane (compound 14~20) are shown in TABLE 2.

Tolane derivatives which have terminal alkenyl group tended to exhibit liquid crystal phases. CN group enhanced the tendency to form nematic phase but

Table2 Physical properties of substituted tolane derivatives



	X_1	X_2	X_3	Y	Phase sequences	Δn [1]
10	CF_3O	H	H	≡	K(121)I	–
11	F	H	H	≡	K(84)I	–[2]
4	C_3H_7	H	H	≡	K(99)I	0.351
12	NC	H	H	≡	K(119)[N(87)]I	0.460
13	NC	F	H	≡	K(109)I	0.414
14	CF_3O	H	H	⟋	K(122)N(127)I	0.303
15	F	H	H	⟋	K(88)I	0.340
16	F	F	H	⟋	K(61)I	0.305
17	F	F	F	⟋	K(34)I	0.270
18	C_3H_7	H	H	⟋	K(73)N(113)I	0.359
19	NC	H	H	⟋	K(100)N(150)I	0.470
20	NC	F	H	⟋	K(74)N(102)I	0.426

[ ] denotes a monotoropic phase
1)Extrapolated Δn values(at 20℃ and λ=589nm) of the mixture (liquid crystal(10wt%) and MJ931381 (90wt%)
2)Insoluble in MJ931381

F and CF_3O groups suppressed liquid crystal phases.

Δn of these compounds were larger than that of conventional tolane (com pound 3) because of extension of π -conjugation by introducing ethynyl or ethenyl group. CN group increased Δn compared with propyl group. But F or CF_3O groups decreased Δn. Δn decreased with the number of F substituent group.

Birefringence and anisotropy of polarizability

The refractive index of nematic phase is expressed as equation (1) and anisotropy of refractive index is propotional to anisotropy of polarizability ($\Delta \alpha$)[8].

$$n_{\parallel}^2 - n_{\perp}^2 = \Delta \varepsilon \propto \Delta \alpha \times S \quad (1)$$

$n_{\parallel}$ and $n_{\perp}$ are refractive index along the molecular long axis and short axis respectively. $\Delta \varepsilon$ is dielectric anisotropy and S is second rank order parameter. We calculated polarizabilities of compounds which were investigated here by MOPAC93. $\Delta \alpha$ was defined as follows.

$$\Delta \alpha = \alpha_{xx} - \frac{(\alpha_{yy} + \alpha_{zz})}{2}$$

α_{xx};Polarizability along the molecular long axis
α_{yy}, α_{zz};Polarizability along the molecular short axis

$n_{\parallel}^2 - n_{\perp}^2$ and calculated $\Delta \alpha$ were plotted in FIGURE 1. The birefringence was almost propotional to $\Delta \alpha$. But the plots showed some scatter. In the case of 1-ring compounds, $n_{\parallel}^2 - n_{\perp}^2$ values were lower than that of 2-ring compounds which have almost same values of $\Delta \alpha$. It is considered that 1-ring compounds have lower order parameters compared with 2-ring compounds therefore $n_{\parallel}^2 - n_{\perp}^2$ were reduced.

Alkynyltolane and alkenyltolane which had substituent F or CF_3O groups also showed lower $n_{\parallel}^2$-$n_{\perp}^2$ than the correspodent non-substituted compounds. $n_{\parallel}^2$-$n_{\perp}^2$ decreased with the increase in the number of F-substituent groups in spite of a little difference in $\Delta \alpha$. It is considered that differences of order parameters of these compounds caused such reduction of Δn. In a binary nematic mixture, order parameters of the two components were predicted not to

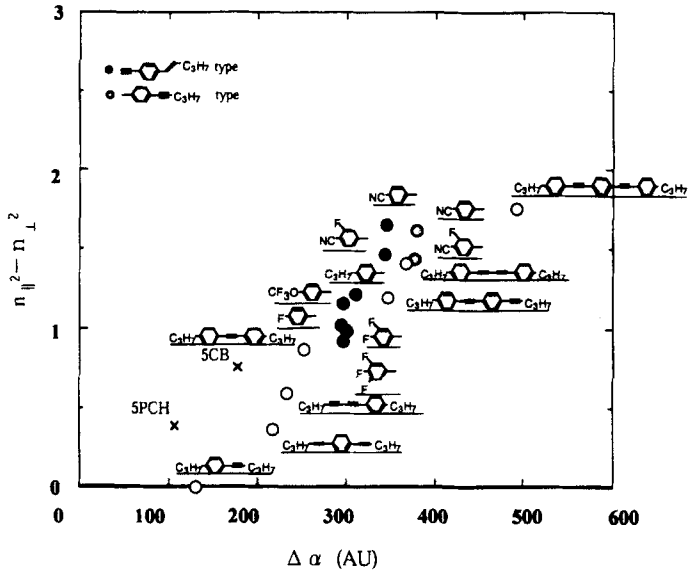


FIGURE1 Plots of Birefringence v.s. Δ α

be equal to each other[9] and it was observed that the order parameters of a compound changed with the concentration of binary mixtures[10]. Concerned with the effect of lateral fluorinated substituents on order parameters, it was confirmed that a non-substituted compound exhibited higer order parameters compared with a laterally fluorinated compound by using C-13NMR[11]. Therefore the Δn of substituted alkenyltolanes and alkynyltolanes were considered to posses different values of order parameters in the mixtures at 20℃ and these compounds which had almost the same Δ α exhibited different values of $n_{\parallel}^2$-$n_{\perp}^2$.

Acknowledgements

A part of this work was performed under the management of Association of Super-Advanced Electronics Technologies (ASET) in the Ministry of International Trade and Industry (MITI) Program of Super-Advanced Electronic

Technolgies supported by New Energy and Industrial Technology Development Organization (NEDO).

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