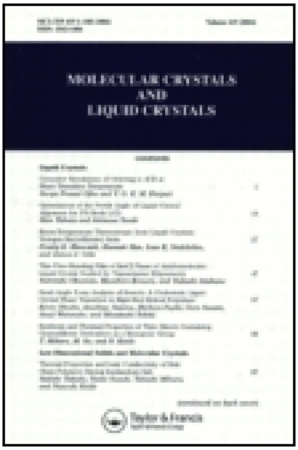

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High Birefringence Phenylacetylene Liquid Crystals with Low Viscosity

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We have synthesized new high Δ n 3-ring phenylacetylene(3PA) liquid crystals which have substituent groups with core center phenyl ring and investigated the effects of substitution on physical properties. Nematic range and viscosity were improved remarkably with keeping high Δ n by introducing trifluoromrthoxy group. The Δ n of 3PAs were also descussed with relationship of polarizability and order parameter.

Keywords: Optical Anisotropy; Anisotropy of Polarizability; High Birefringence; Low Viscosity; Phenylacetylene

INTRODUCTION

Liquid crystals with high birefringence (Δn) are useful components of liquid crystal mixtures. They are empolyed for the conventional super twisted nematic(STN) devices as a Δn moderator. The setting value of Δn is around 0.15 so that moderate Δn liquid crystals are contained in the mixtures. Recently with remarkable development of multimedia technology, a strong demand for high perfoemance mobile display has been created and higher Δn liquid crystals have bewen investigated for applications to PDLC, spatial moduratots and new components of

LCDs[1],[2].

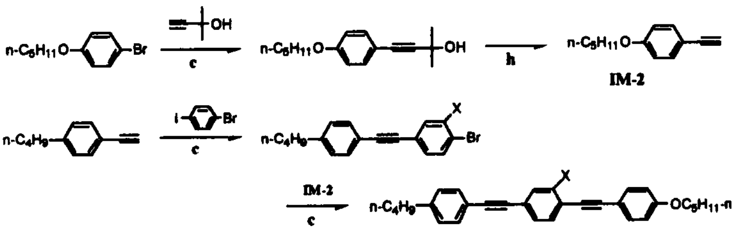
It is well known that high Δn can be achieved by increasing the molecular conjugation length[3]. We have been developed very high Δn liquid crystals which were phenylacetylene homologues as a highly conjugated molecules along the molecular long axis[4][5]. They exhibited high Δn as expectation, but they were not suitable for practical use because of high nematic range and poor solubility. We modified 3-ring phenylacetylene(3PA) compounds and it was found that introducing methyl group to the core center ring was effective for improving these problems[6][7]. In this study we synthesized 3PAs with different type of substituent groups and investigated the effects of them on the physical properties.

EXPERIMENTALS

SYNTHESIS

The synthesis routes of phenylacetylene derivatives are shown in SCHEME 1 ~ 4. Compound **1a** and **3a** were synthesized by coupling of bromided intermediates and ethynyl intermediates. Other compounds were synthesized by coupling of trifluoromethoxysulphonic acid intermediates with ethynyl intermediates.

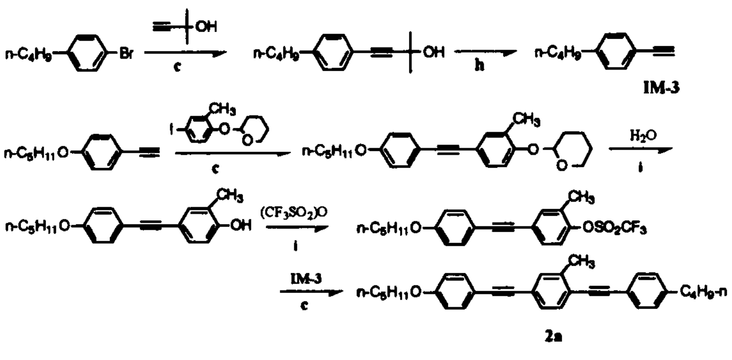
The structures of final compounds and various synthetic intermediates



X=H; **1a**, X=OCF$_3$; **3a**

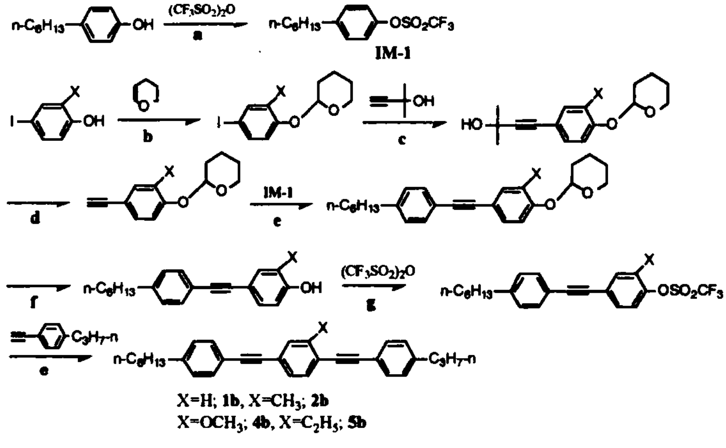
c; $PdCl_2(PPh_3)_2$ /PPh_3 /CuI / triethylamine, h; NaOH/Toluene

SCHEME1 Syntheses of substituted 3-ring phenylacetylene(3PA) s



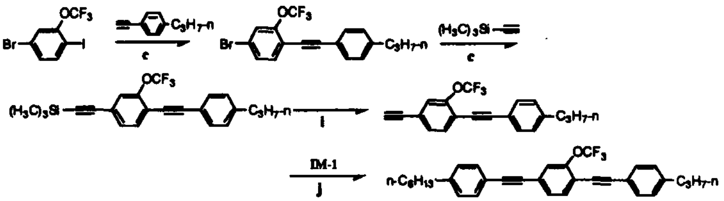
c; PdCl2(PPh 3)2 /PPh 3 /CuI / triethylamine, i; p-Toluenesulphonnic acid

SCHEME2 Syntheses of 3PA derivatives(2)



c; PdCl2(PPh 3)2 /PPh 3 /CuI / triethylamine, i; p-Toluenesulphonnic acid, j; PdCl2(PPh 3)2/ triethylamine
g; pyridine/4-pyrorinopyridine

SCHEME3 Synthesis of substituted 3PA derivatives(3)



a; pyridine/4-pyrorinopyridine, b; p-toluenesulfonic acid, c; PdCl$_2$(PPh$_3$)$_2$ /PPh$_3$ /CuI /triethylamine, d; toluene/KOH, e; PdCl$_2$(PPh$_3$)$_2$/triethylamine/DMF, f; p-toluenesulfonic acid/methanol,

SCHEME4 Synthesis of substituted 3PA derivatives(4)

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 confirmed using DSC (DSC-200 ,Seiko Instruments Inc.).

Refractive index was evaluated as exrapolated 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°C. A sodium lamp was used to provide the light source at 589nm. Birefringence of single compounds were also measured. A parallel aligned wedge cell was used for the measurement. Each reflection angle of the incident He-Ne laser (λ=633nm) light polarized parallel and perpendicular to the rubbing direction were measured for calculation of no and ne. Order parameters were estimated by measureing of polarized IR absorption spectra(FT-IR, Magna860,Nicolet). 10μm thick homogeneously aligned cells were prepared for this measurement. The substrates were CaF$_2$ crystal plates coated with polyimide(LX-1800, Hitach Chemical,)and rubbed one direction. Order parameters were calculated from the dicroic ratio[8] of the acetylene C-C strching absorption peaks of the compounds.

$S=(D+1)/(D-2)$ D; Dicroic ratio, S;Order parameters

Viscosity was measured by maicroviscometer(AMV-200, DMA48 for the measurement of density, Anton Parr KG). The samples used for this measurement were the same mixtures of Δn evaluations.

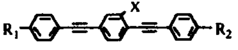
RESULTS AND DISCUSSIONS

Influences of substituent groups on physical properties

The phase sequences and transition temperatures of compounds **1a**~**3a** and **1b**~**5b** are listed in TABLE1. The nematic range was lowered by introducing a substituent methyl group to the core center phenylene ring. The effect was more pronounced by substitution of trifluoromethoxy or ethyl groups. Compound **5b** exhibited nematic phase at room temperature. In the case of methoxy group melting point increased so that the nematic range was narrower than those of another type compounds.

Δn of 3PAs estimated from the mixtures were also lited in TABLE1.

TABLE1 Physical proprties of phenylacetylene derivative

				Transition temperatures [°C]	Optical anisotropy[1]			Viscosity[2] [mPas]
	R1	R2	X		no	ne	Δn	
1a	$C_5H_{11}O$	C_4H_9	H	K・162・N・234・I	1.519	1.966	0.448	—
2a	$C_5H_{11}O$	C_4H_9	CH_3	K・83・N・201・I	1.525	1.955	0.430	156
3a	$C_5H_{11}O$	C_4H_9	OCF_3	K・60・N・127・I	1.502	1.875	0.374	100
1b	C_6H_{13}	C_3H_7	H	K・147・N・209・I	1.515	1.947	0.432	84
2b	C_6H_{13}	C_3H_7	CH_3	K・57・N・169・I	1.524	1.944	0.419	119
3b	C_6H_{13}	C_3H_7	OCF_3	K・34・N・85・I	1.498	1.844	0.346	56
4b	C_6H_{13}	C_3H_7	OCH_3	K・86・N・108・I	1.534	1.923	0.389	353
5b	C_6H_{13}	C_3H_7	C_2H_5	K・16・N・115・I	1.528	1.907	0.379	94

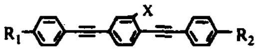
1) Extrapolated values(at 20°C and λ=589nm) of the mixture [liquid crystal(10wt%) and MJ931381 (90wt%)]
2) Extrapolated values(at 20°C) of the mixiure [liquid crystal(10wt%) and MJ931381 (90wt%)]

These compounds exhibited very high Δn around 0.4. Δn was decreased by the substituent groups as $H>CH_3>C_2H_5>OCF_3>OCH_3$. Visocity of these serires are slightly high compared with conventional 2-ring type liquid crystals. Introducing substituent groups increased viscosity, but trifluoromethoxy group decreased the viscosity remarkably. The viscosity of trifluoromethoxy type was lower than ethyl, methoxy or non-substituted type. It was considered that not only bulkiness of substituent group but also fluorine atoms reduced the interaction of molecules and induced lower viscocious property.

Birefringence and anisotropy of polarizability

Temperature dependenceof Δn and order parameter(S) of single materials are also measured and the values at T_{NI}-T=100 are listed in TABLE2. Δn and S were reduced by introducing substituent groups, but trifluoromethoxy group did not affect these properties. Introducing non-polar substituent group to the rateral positon increased the free volume of the molecule so that it may caused mobility along n-director to increase and S to decreased. But in the case of polar substituent group as

TABLE2 Comparison of experimental and calculated Δn



	R1	R2	X	Δn(exp)[1]	S[1]	α[2]	Δα[3]	Δn(calc)[4]
1a	$C_5H_{11}O$	C_4H_9	H	0.383	0.76	359	525	0.580
2a	$C_5H_{11}O$	C_4H_9	CH_3	0.363	0.70	368	522	0.484
3a	$C_5H_{11}O$	C_4H_9	OCF_3	0.382	0.76	378	525	0.492
1b	C_6H_{13}	C_3H_7	H	0.363	0.76	349	502	0.560
2b	C_6H_{13}	C_3H_7	CH_3	0.361	0.70	358	499	0.467
3b	C_6H_{13}	C_3H_7	OCF_3	0.363	0.77	366	494	0.473
4b	C_6H_{13}	C_3H_7	OCH_3	0.339	0.59	363	494	0.389
5b	C_6H_{13}	C_3H_7	C_2H_5	0.362	0.69	366	489	0.434

1)Experimental datas at T_{NI}-T=100
2) $\alpha=(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})/3$
3) $\Delta\alpha=\alpha_{xx}-(\alpha_{yy}+\alpha_{zz})/2$
4)Calculated by Vucks low

trifluoromethoxy, the interaction of core part covered the effect of increasing free volume. As a result S was not almost affected.

For the consideration of effects of substituent groups on Δn, it was calculated using the equation proposed by Vuck[9].

$$\frac{ne^2-1}{n^2+2} = \frac{N}{3\varepsilon_0}\left(\alpha + \frac{2\Delta\alpha S}{3}\right) \qquad (1)$$

$$\frac{no^2-1}{n^2+2} = \frac{N}{3\varepsilon_0}\left(\alpha - \frac{\Delta\alpha S}{3}\right) \qquad (2)$$

where $n^2=(ne^2+2no^2)/3$. $\Delta\alpha$ denotes anisotropy of the molecular polarizxability α. S is order parameter, ε_0 is the static dielectric constat and N is tne number of moleculed per unit volume. $\Delta\alpha$ and α were calculated by MOPAC93(AM1 method) for the isolated molecule. Number density was approximared using the group contribution method of Fedors[10]. The tendency of effects of substituent group on experimental Δn was almost same as calculated ones. $\Delta\alpha$ and α were not affected by substituent groups. Therefore the decrease of Δn by substituting methyl, ethyl and methoxy groups was caused by decreasing of order parameters.

Δn estimated from extrapolation of 10%mixtures were polted vs calcu lated ones in FIGURE1. It was considered that there was not

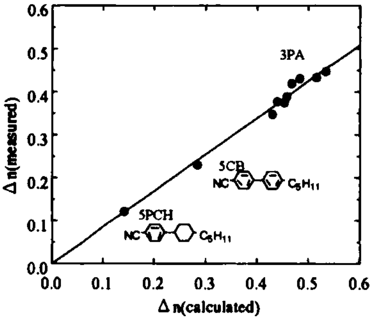


FIGURE1. Plots of experimental vs calculated of Δn

difference so much in order parameters bwteen these compouns in the mixture. S of 0.7 was assumed for the calculations. For reference in the area of low birefringence 5CB and 5PCH were also plotted. The experimental and calculated Δn showed good proportional relationship. Therefore Δn was determined by order parameter and nember density with respect to these series.

CONCLUSION

We have synthesized and evaluated substitued 3 ring phenylacetylene homologes with substituent groups to core center phenylring. Introduing trifluoromrthoxy group was effective for lowering nematic range and ciscosity. Therefore this type compound was useful for preparing of practical liquid crystal mixtures.

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