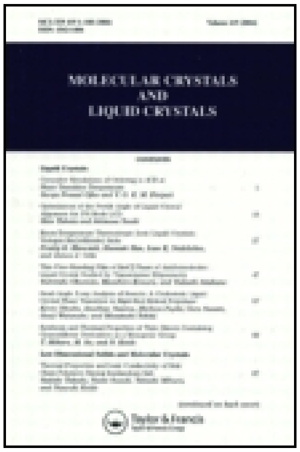

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Physical Properties of Nematic Tolans

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Physical Properties of Nematic Tolans

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A series of 4-n-alkyl-4′-n-alkoxytolans, trans-4-n-alkylcyclohexyl-4′-n-alkyltolans and 4-n-alkyl-2′- or 3′-substituted 4′-n-alkoxytolans was prepared. Their mesomorphic and physical properties were measured. Some nematic mixtures of 4-n-alkyl-4′-n-alkoxytolans and other familiar series of nematic mixtures of two-ring systems having n-alkyl and n-alkoxy as terminal groups were prepared and their physical properties were compared. A nematic mixture of tolans has a high N-I transition temperature of 72°C, a high birefringence of 0.297 and a low viscosity of 19.1 c.p. at 20°C. The birefringence and the flow-aligned viscosity of trans-4-n-propylcyclohexyl-4′-n-butyltolan were determined by extrapolation and compared with those of trans-4-n-pentylcyclohexyl-4′-ethylbiphenyl and 4-n-propylphenyl 4′-n-propylcyclohexyl-benzoate. The influence of the introduction of 2′-, 3′-fluoro and 2′-, 3′-methyl groups into 4-n-alkyl-4′-n-alkoxytolans on the dielectric constants was discussed.

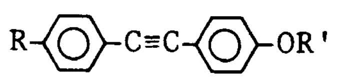
Keywords: liquid crystal, nematic, tolans

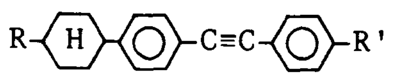
INTRODUCTION

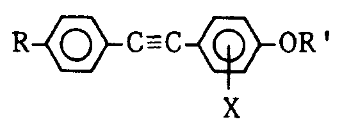
The response time for TN-LCDs is almost proportional to the viscosity (η) and the second power of the cell thickness (d^2).[1] The product of the birefringence and the cell thickness (Δnd) should be fixed to certain values in order to achieve a good cell appearance.[2] Therefore, nematic compounds of low viscosity and high birefringence are required for quick response time.

Some hydrocarbons[3] have the effect of reducing the viscosity and the *N-I* transition temperature is reduced remarkably. We reported[4] that an ethylenic group effectively raises the *N-I* transition temperature and the birefringence. The nematic trans-phenylethylenes, however, are isomerized to cis-phenylethylenes by UV irradiation and cannot be applied to TN-LCDs.

We have synthesized the 4-n-alkyl-4′-n-alkoxyltolans of formula (I), which were originally reported[5] by Jacques *et al.* in 1971, and other nematic tolans of formula (II) and formula (III), including an acetylenic group, in order to achieve nematic mixtures having high birefringence and low viscosity with a high N-I transition temperature and to discuss the effect of lateral substituents on the physical properties.


(I)


(II)


(III)

R, R' = n-alkyl

X = CH_3 - or F

PREPARATION OF MATERIALS

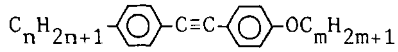
The tolans were prepared by the coupling of n-alkylphenyl-acetylenes and the corresponding iodides. The compounds of formula (I) and formula (III) were distilled and purified by recrystalization from alcohol. The compounds of formula (II) were purified by recrystalization from n-hexane and alcohol. The purity was tested by high pressure liquid chromatography and gas-liquid chromatography. Each product was identified by NMR spectrometry and mass spectrometry.

RESULTS AND DISCUSSION

The transition temperatures and the transition enthalpies for the 4-n-alkyl-4′-n-alkoxytolans are listed in Table I. The nematic mixture A of tolans and other familiar series of nematic mixtures (B~H) of

TABLE I

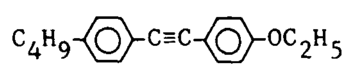
Transition temperatures and transition enthalpies of 4-n-alkyl-4′-n-alkoxytolans

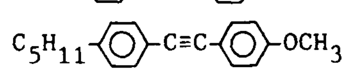


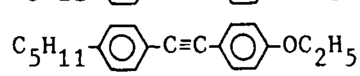
n	m	Transition temp. (°C) C-N	Transition temp. (°C) N-I	ΔH (kcal/mol) C-N	ΔH (kcal/mol) N-I
3	2	89	96	4.96	0.163
3	5	55	70	3.29	0.110
4	2	54	80	5.64	0.167
5	1	47	58	4.29	0.138
5	2	62	89	5.55	0.234
5	5	51	70	3.75	0.156

two-ring systems having n-alkyl and n-alkoxy as terminal groups were prepared. Their compositions and properties are shown in Table II and their N-I transition temperatures, flow-aligned viscosities and birefringences are compared in Figure 1 and Figure 2 to evaluate their usefulness. They show that the mixture A of tolans has a high N-I transition temperature, a low flow-aligned viscosity and a high birefringence compared with other series of mixtures. The nematic mixture A1 has a high birefringence of around 0.3 and a flow-aligned viscosity below 20 c.p. at 20°C. The nematic mixture A2, including 4-n-alkyl-4′-n-alkyltolans, shows quite a low viscosity of 16.4 c.p. at 20°C. The compositions and physical properties of mixture A1 and mixture A2 are as follows:

Mixture A1

Compositiob: 30 wt% of 

40 wt% of 

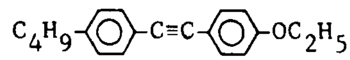
40 wt% of 

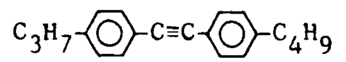
Nematic range: 32 ∼ 72°C

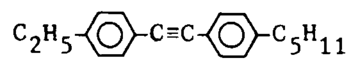
Flow-aligned viscosity: 19.1 c.p. at 20°C

Birefringence: 0.297 at 25°C

Mixture A2

Composition: 50 wt% of 

25 wt% of 

25 wt% of 

Nematic range: 33 ~ 47°C

Flow-aligned viscosity: 16.4 c.p. at 20°C

Birefringence: 0.231 at 25°C

The flow-aligned viscosities at 20°C were determined by extrapolation and the birefringences were measured in the super-cooled state.

The transition temperatures of trans-4-n-alkylcyclohexyl-4′-n-alkyltolans are shown in Table III. The flow-aligned viscosity at 20°C and birefringence of trans-4-n-propylcyclohexyl-4′-butyltolan are de-

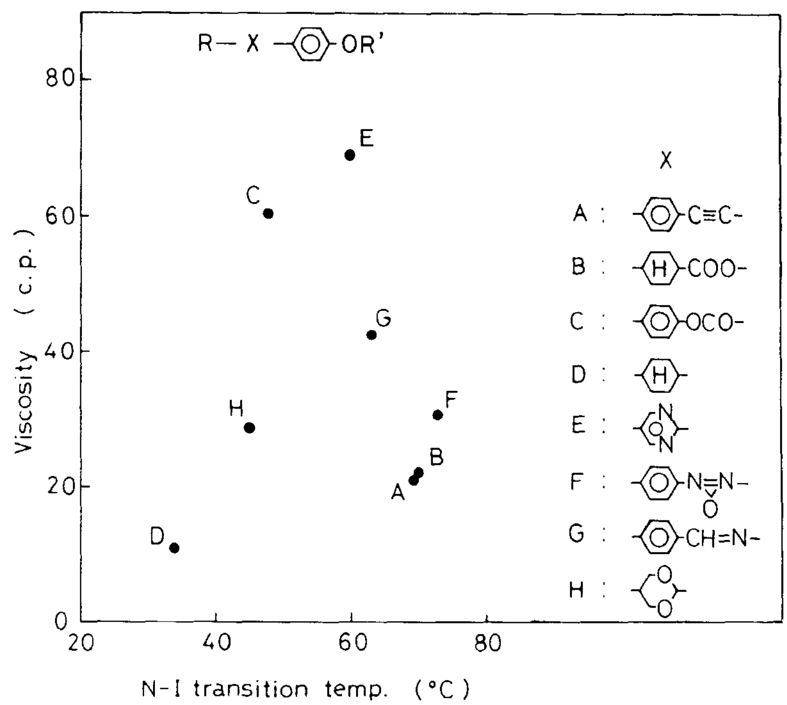


FIGURE 1 Flow-aligned viscosity vs. n-1 transition temperature for various series of nematic mixtures with alkyl and alkoxy groups as terminal groups.

groups

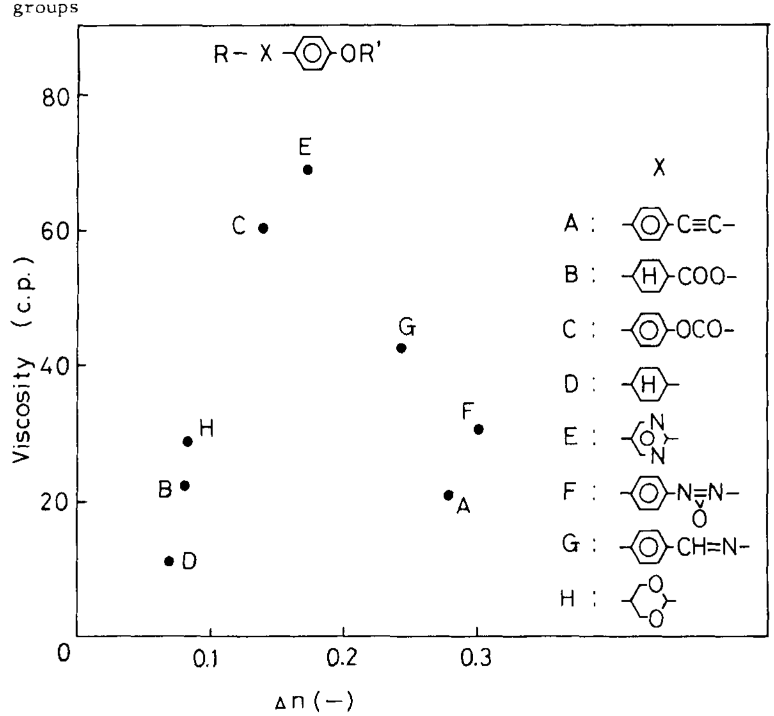


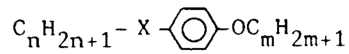
FIGURE 2 Flow-aligned viscosity vs. birefringence for various series of nematic mixtures with alkyl and alkoxy groups as terminal groups.

termined by an extrapolation method similar to that mentioned in a previous paper[6] and compared with those of other nematic compounds having a cyclohexyl and two phenylene rings in Table IV. The results show that the acetylenic group as a linkage between two phenylene rings increases the N-I transition temperature and birefringence remarkably and does not increase the flow-aligned viscosity so much.

The transition temperatures of 2- or 3-substituted tolans and the dielectric constants are shown in Table V and Table VI, respectively. The introduction of the 2-fluoro group decreases the N-I transition temperature by about 25°C, decreases the C-N transition temperature a little and increases the dielectric constant parallel ($\epsilon\|$) and perpendicular ($\epsilon\perp$) to the optical axis and the dielectric anisotropy ($\Delta\epsilon$). The introduction of the 2-methyl group decreases the N-I transition temperature by about 35°C and the C-N transition temperature by 20°C in the case of $n=5$, $m=2$. It slightly increases $\epsilon\|$ and $\epsilon\perp$ and

TABLE II

Physical properties of a mixture of tolans and familiar series of nematic mixtures containing two-ring systems



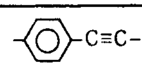
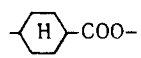
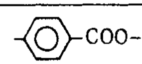
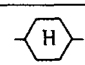
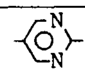
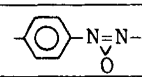
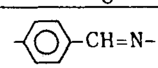
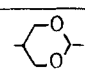
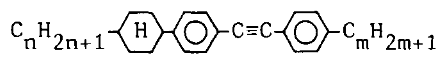
Mixture	Series	X	Component (n,m) %	Nematic range (°C)	Δn (−)	Viscosity at 20°C (c.p.)
A	Tolans		(5,1)40, (4,2)40, (3,5)20	23 ∼ 68	0.277	21.0
B	Cyclohexane carboxylates		(5,1)40, (4,2)40, (3,5)20	20 ∼ 70	0.0804	22.1
C	Esters		(5,1)67, (5,6)33	15 ∼ 48	0.137	60.3
D	Phenyl cyclohexanes		(3,2)50, (3,4)50	18 ∼ 34	0.0695	11.1
E	Pyrimidines		(6,6)68, (6,9)32	10 ∼ 60	0.171	68.8
F	Azoxys		(4,1)66, (2,1)34	-5 ∼ 73	0.300	30.6
G	Azomethynes		(4,1)36, (4,2)40, (4,4)24	-10 ∼ 63	0.242	42.5
H	Dioxanes		(3,2)30, (4,2)30 (7,2)40	33 ∼ 45	0.0830	28.7

TABLE III

Transition temperatures of 4-n-alkylcyclohexyl-4′-n-alkoxytolans



n	m	Transition temp. (°C) C-N	Transition temp. (°C) N-I
2	3	86	189
3	2	108	208
3	3	96	213
3	4	87	201
4	1	87	202
4	2	102	197
4	3	97	202

decreases $\Delta\epsilon$. The introduction of the 3-fluoro and 3-methyl groups reduces the tendency of exhibiting nematic phases remarkably. It shows that the 3-substituent much influences the molecular interaction. The introduction of the 3-fluoro group increases $\epsilon\|$ and $\epsilon\perp$ and decreases 0.3 $\Delta\epsilon$. The introduction of the 3-methyl group slightly increases $\epsilon\|$, $\epsilon\perp$ and $\Delta\epsilon$.

TABLE IV

N-I transition temperatures ($T_{N\text{-}I}$), flow-aligned viscosities at 20°C ($\eta_{20°C}$) and birefringences at 25°C (Δn) of trans-4-n-propylcyclohexyl-4′-n-butyltolan and other nematic compounds, including a cyclohexyl and two phenylene rings

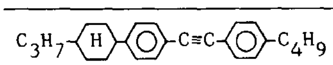
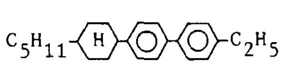
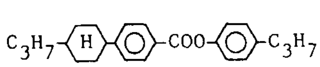
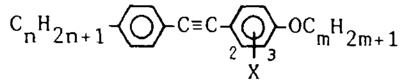
Formula	T_{N-I} (°C)	$\eta_{20°C}$ (c.p.)	Δn (—)
	201	47.9	0.253
	164	33.6	0.171
	186	83.6	0.163

TABLE V

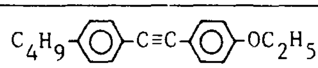
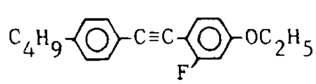
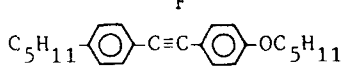
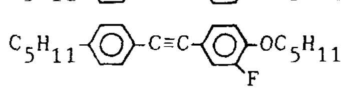
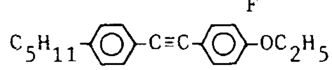
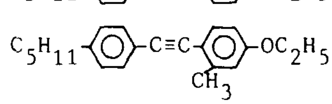
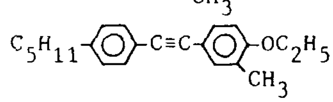
Transition temperatures of 2- or 3-substituted tolans



n	m	X	Position (2 or 3)	Transition temp. (°C) C	N	I
3	2	F	2	· 70	(· 70	·
4	2	F	2	· 45	· 51	·
4	2	F	3	· 56	–	·
5	2	F	2	· 61	· 66	·
5	5	F	3	· 40	(· 35	·
4	2	CH_3	2	· 58	(· 42	·
4	2	CH_3	3	· 55	–	·
5	2	CH_3	2	· 42	· 54	·
5	2	CH_3	3	· 70	(· 45	·

TABLE VI

Dielectric constants of tolan derivertives

Formula	Dielctric constants (–) $\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
	3.3	3.2	+0.1
	4.8	4.4	+0.4
	3.2	3.0	+0.2
	4.1	5.1	-1.0
	3.2	3.0	+0.2
	3.5	3.5	+0.0
	3.8	3.3	+0.5

Acknowledgments

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5. J. Jacques, U.S. Patent 3,925,482 (1975).
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