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Liquid crystals of some new tolane derivatives containing a 1,2-ethylene linkage

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Liquid crystals of some new tolane derivatives containing a 1,2-ethylene linkage

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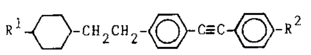
Three types of nematogenic compound, 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltolanes, 2-fluoro-4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltolanes and 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-halogenotolanes, have been synthesized and their transition temperatures and enthalpies determined. Their bulk viscosity and birefringence have been estimated from those of mixtures with other liquid-crystalline compounds. These compounds have been found to be excellent materials for twisted nematic displays, because of their wide nematic temperature range, high birefringence ($\Delta n = 0{\cdot}26$), and low viscosity ($\eta = 21$ cP at 20°C). Several related compounds having other central linkages, namely $-CH_2O-$, a single bond or $-COO-$, in place of the 1,2-ethylene group, have also been studied.

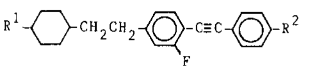
1. Introduction

Nematogenic materials of low viscosity and high birefringence with acceptably wide mesomorphic temperature ranges are needed for twisted nematic liquid-crystal displays [1, 2]. Tolane derivatives and some compounds with a pyrimidine ring have so far been reported to have such properties [3–6].

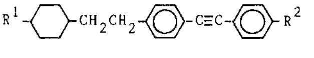
We now report three types of tolane derivatives with a tricyclic structure containing the 1,2-ethylene linkage ($-CH_2CH_2-$), namely 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltolanes (I), 2-fluoro-4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltolanes (II) and 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-halogenotolanes (III):



(R^1, R^2 = alkyl) (I)



(R^1, R^2 = alkyl) (II)



(R^1 = alkyl, R^2 = halogen) (III)

2. Results and discussion

(i) The transition temperatures, birefringence (Δn at 25°C), viscosity (η at 20°C) and transition enthalpy for melting (ΔH_{melt}) for the compounds (I) are shown in table 1, and the transition temperatures are plotted against the number of carbon atoms in the alkyl chain in figure 1. The usual odd–even effects are seen for the C–N and N–I transitions as well as ΔH_{melt} (see table 1). These compounds have an extended liquid-crystal range with a high birefringence and a low viscosity. The thermodynamic stability of the smectic phase increases with the chain lengths of R^1 and R^2 as usual, but the smectic–nematic transition shows an unusual odd–even effect, i.e. even-numbered chains give a higher S–N curve than the odd-numbered ones. The Δn and η values, which are estimated by extrapolation, do not show an apparent trend depending on the chain length. The physical properties of mixture composed of

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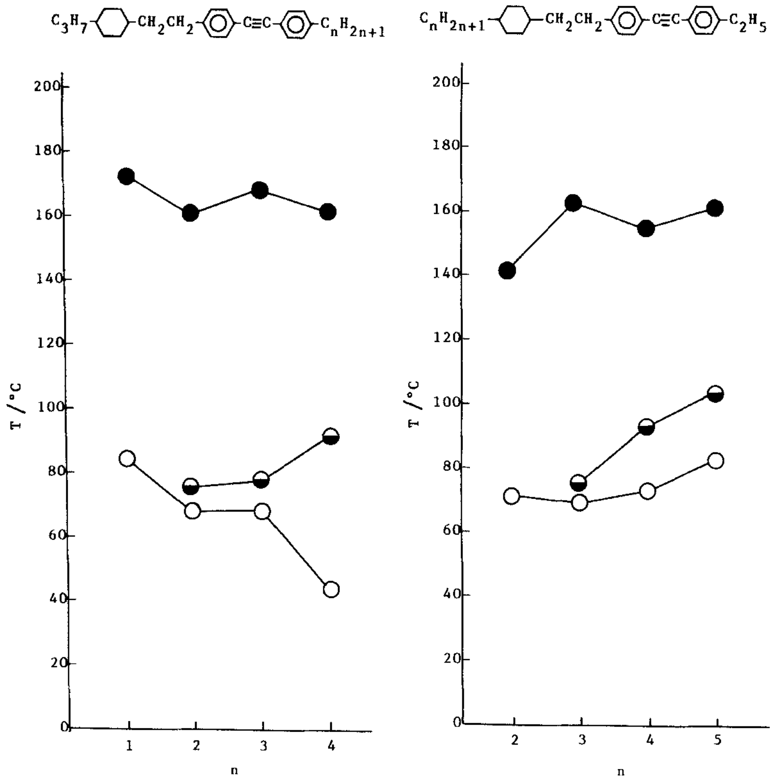


Figure 1. Plot of transition temperatures versus alkyl chain length for the series of 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltonanes: ○, crystal–nematic or crystal–smectic transition; ◒, smectic–nematic transition; ●, nematic–isotropic transition.

Table 1. Transition temperatures (°C), birefringence, viscosity and transition enthalpy for the series of 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltolanes (I).

No.	R^1	R^2	C		S		N		I	Δn	η_{20}/cP	ΔH_{melt}/kJ mol^{-1}
1	C_2H_5	CH_3	●	84·3			●	144·5	●	0·241	22·3	15·99
2	C_2H_5	C_2H_5	●	69·4			●	141·2	●	0·239	21·8	14·36
3	C_2H_5	C_3H_7	●	66·1			●	150·1	●	0·232	21·5	8·04
4	C_2H_5	C_3H_7	●	59·1	●	62·3	●	137·3	●	0·231	22·6	7·03
5	C_3H_7	CH_3	●	83·6			●	169·1	●	0·258	22·1	13·52
6	C_3H_7	C_2H_5	●	68·7	●	74·1	●	161·8	●	0·266	21·4	12·56
7	C_3H_7	C_3H_7	●	67·1	●	77·6	●	166·6	●	0·259	21·7	12·14
8	C_3H_7	C_4H_9	●	42·5	●	90·0	●	158·8	●	0·248	22·7	6·62
9	C_4H_9	CH_3	●	85·6	(●	77·8)	●	162·3	●	0·251	22·1	16·41
10	C_4H_9	C_2H_5	●	69·5	●	92·7	●	155·7	●	0·258	21·5	11·85
11	C_4H_9	C_3H_7	●	65·6	●	94·2	●	161·6	●	0·260	22·0	10·09
12	C_4H_9	C_4H_9	●	59·8	●	103·1	●	152·5	●	0·232	22·4	8·58
13	C_5H_{11}	CH_3	●	91·7	(●	85·6)	●	165·3	●	0·258	21·8	14·44
14	C_5H_{11}	C_2H_5	●	81·5	●	100·4	●	158·0	●	0·249	21·8	12·23
15	C_5H_{11}	C_3H_7	●	67·9	●	112·1	●	165·4	●	0·256	21·6	8·29
16	C_5H_{11}	C_4H_9	●	55·2	●	119·1	●	156·3	●	0·236	22·4	6·91

C, solid phase; S, smectic phase; N, nematic phase; I, isotropic phase. Monotropic transition temperatures are shown in brackets. Birefringence and viscosity are extrapolated values.

15 wt % of compound (I) and 85 wt % of the PCH mixtures S-1083 (E. Merck) are shown in table 2. Four compounds of type (I), namely $R^1 = C_2H_5$ $R^2 = C_2H_5$, $R^1 = C_2H_5$ $R^2 = C_3H_7$, $R^1 = C_3H_7$ $R^2 = C_2H_5$, $R^1 = C_3H_7$ $R^2 = C_3H_7$, were mixed in equal weights. This mixture (A) was mixed with varied amounts of S-1083 to obtain several mixtures. Their nematic–isotropic transitions, log η and Δn are plotted against composition in figure 2. It is evident from these data that the compounds (I) have a prominent characteristic of substantially raising the N–I transition and Δn, while decreasing η, when added to S-1083 for example.

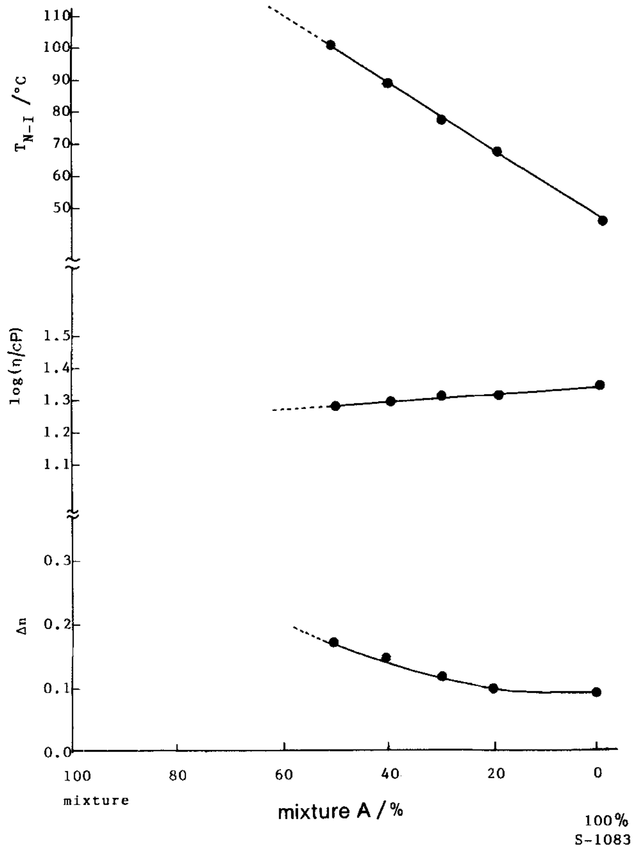


Figure 2. The nematic–isotropic transition temperatures, the logarithm of the viscosity and the birefringence for S-1083 : mixture A system.

(ii) The properties of the compounds are shown in table 3. Here again the odd–even effects are seen for C–N and N–I transitions. The introduction of a fluorine atom suppresses the stability of the smectic phase, reduces the nematic–isotropic transition by 10–15°C, and reduces the melting points (C–N or C–S points) by 17–33°C. As a result, the nematic range is extended by 5–22°C compared with the unsubstituted compounds (I); compare the fluorine-substituted compound No. 18 with the unsubstituted counterpart compound No. 4, for example, where the nematic temperature range is extended by 22°C. The extrapolated value of Δn is unaltered, but the extrapolated viscosity is increased by the introduction of a lateral fluorine atom.

Table 2. Physical properties of a mixture of compound (I) 15 wt % with S-1083 85 wt %.

R^1R^2	C_2H_5/C_2H_5	C_2H_5/C_3H_7	C_2H_5/C_4H_9	C_3H_7/C_2H_5	C_3H_7/C_3H_7	C_3H_7/C_4H_9	S-1083
$T_{NI}/°C$	64·1	64·8	63·7	67·9	68·0	67·1	52·1
η_{20}/cP	2·0	22·1	22·2	21·6	22·0	22·0	22·4
Δn (25°C)	0·135	0·135	0·132	0·139	0·141	0·137	0·119

Table 3. Transition temperatures (°C), birefringence, viscosity and transition enthalpy for the series of 2-fluoro-4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-alkyltolanes (II).

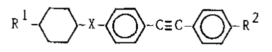
No.	R^1	R^2	C		S		N		I	Δn	η_{20}/cP	ΔH_{melt}/kJ mol^{-1}
17	C_2H_5	C_2H_5	●	50·6			●	166·9	●	0·239	28·3	14·49
18	C_2H_5	C_3H_7	●	36·0			●	135·2	●	0·239	29·8	12·35
19	C_2H_5	C_4H_9	●	26·1			●	126·5	●	0·266	29·7	9·71
20	C_3H_7	CH_3	●	73·2			●	158·3	●	0·259	27·3	24·41
21	C_3H_7	C_2H_5	●	50·8			●	149·8	●	0·252	27·3	14·11
22	C_3H_7	C_3H_7	●	50·2			●	155·5	●	0·252	27·1	20·10
23	C_3H_7	C_4H_9	●	42·0			●	148·6	●	0·239	27·4	15·45
24	C_4H_9	C_2H_5	●	58·3			●	147·8	●	0·258	28·3	15·37
25	C_4H_9	C_3H_7	●	56·5	(●	43·5)	●	155·1	●	0·249	29·2	18·51
26	C_4H_9	C_4H_9	●	50·4	●	71·8	●	147·1	●	0·245	29·3	14·99

Table 4. Transition temperatures (°C), birefringence, viscosity and transition enthalpy for the series of 4-[2-(*trans*-4-alkylcyclohexyl)ethyl]-4′-halogenotolanes (III).

No.	R^1	R^2	C		S		N		I	Δn	η_{20}/cP	ΔH_{melt}/kJ mol^{-1}	$\Delta\varepsilon$ (25°C)
27	C_3H_7	F	●	85·8	(●	63·6)	●	148·8	●	0·226	22·1	27·60	8·0
28	C_4H_9	F	●	75·1	●	78·0	●	145·8	●	0·219	22·4	28·39	7·4
29	C_5H_{11}	F	●	78·7	(●	75·6)	●	149·8	●	0·219	22·4	31·69	7·4
30	C_3H_7	CL	●	103·1			●	177·4	●	0·234	36·8	26·80	10·6

(iii) The transition temperatures and other physical properties of the compounds (III) are shown in table 4. The dielectric anisotropy $\Delta\varepsilon$ of these compounds is about $+7$ because of the terminal halogen atom, in contrast with that of the alkyl compounds (I) and (III), where $\Delta\varepsilon$ is nearly zero. The compounds (III) give nearly the same Δn and η, but higher melting points and ΔH_{melt} compared with the compounds (I) and (II).

(iv) The modification of chemical structure (I) were made by replacing the 1,2-ethylene linkage with a single bond, methyleneoxy ($-CH_2O-$) and carboxy ($-COO-$) groups, to obtain the general structure (IV).



(IV) X = single bond, $-CH_2O-$, $-COO-$

The physical properties of these compounds, together with some of the compounds (I) (i.e. X = $-CH_2CH_2-$ in (IV)) for ease of comparison are listed in table 5. The results may be summarized as follows.

(*a*) the melting point (C–N or C–S transition) decreases in the order $-CH_2O- >$ single bond $> -COO- > -CH_2CH_2-$;

(*b*) the N–I transition decreases in the order single bond $> -COO- > -CH_2O- > -CH_2CH_2-$;

(*c*) the incidence of a smectic phase is observed for the $-CH_2O-$ and $-CH_2CH_2-$ linkages.

The extrapolated values of η and Δn, for the $R^1 = R^2 = C_3H_7$ members of these four series, are plotted in figure 3. As to the η values, $-CH_2CH_2-$ is superior to the others (lower), while Δn of the tolane core is relatively insensitive to the variation of X, as expected.

Table 5. Transition temperatures (° C) for four series of three-ring nematogenic compounds containing different linkages X.

Series	X	R^1	R^2	C		S		N		I	Source
1	single bond	C_3H_7	C_2H_5	●	108·0			●	208·0	●	[4]
		C_3H_7	C_3H_7	●	96·0			●	213·0	●	
		C_3H_7	C_4H_9	●	87·0			●	201·0	●	
2	$-CH_2CH_2-$	C_3H_7	C_2H_5	●	68·7	●	74·1	●	161·8	●	this work
		C_3H_7	C_3H_7	●	67·1	●	77·6	●	166·6	●	
		C_3H_7	C_4H_9	●	42·5	●	99·0	●	158·8	●	
3	$-CH_2O-$	C_2H_5	C_2H_5	●	120·3			●	163·7	●	[7]
		C_2H_5	C_3H_7	●	153·6	●	155·8	●	196·1	●	
		C_3H_7	C_3H_7	●	148·2	●	179·4	●	210·3	●	
4	-COO-	C_3H_7	C_3H_7	●	110·4			●	133·5	●	[8]
		C_3H_7	C_4H_9	●	89·8			●	212·9	●	
		C_3H_7	C_5H_{11}	●	93·8			●	212·4	●	

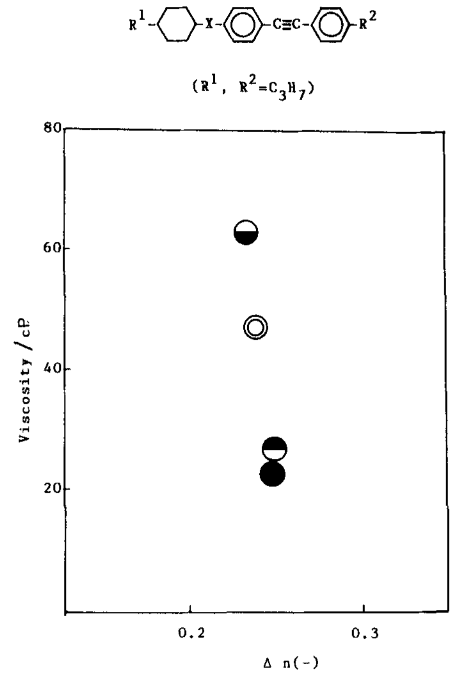


Figure 3. Viscosity versus birefringence for four series of nematogenic compounds containing three ring systems: ◒, x = $-CH_2O-$; ◎, -COO- ◓, covalent bond; ●, $-CH_2CH_2-$.

3. Experimental procedure

3.1. *Identification*

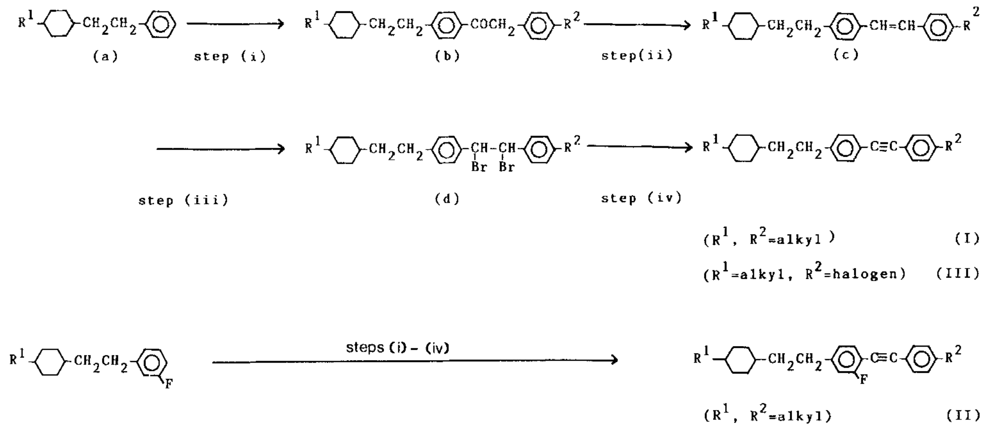
The final samples of the compounds were all confirmed to have a purity greater than 99·8 per cent using gas–liquid chromatography (G.L.C.) and high-performance liquid chromatography (H.P.L.C.). The infrared and H N.M.R. spectra were used for identification. Infrared spectra were measured with a Hitachi 260-10 spectrometer and the N.M.R. spectra with a Jeol JNM-EX90 spectrometer.

3.2. *Transition temperatures, birefringence, viscosity and transition enthalpy*

The transition temperatures were determined with a polarizing microscope, Nikon optiphoto-pol, equipped with a Mettler hot stage FP52 and control unit FP5, the birefringence with a microrefractometer, the viscosity with a rotary viscosimeter, and the enthalpy with a differential-scanning calorimeter, Rigaku-8230.

3.3. *Synthesis*

The compounds (I), (II) and (III) were synthesized by the routes shown in scheme 1. The products were purified by column chromatography using silica gel as the stationary phase and methylene chloride: hexane mixture (1 : 5 v/v) as eluant, followed by crystallization until constant liquid-crystal transition temperatures were obtained.



step (i) 4-alkylphenylacetyl chloride, $AlCl_3$, CS_2
step (ii) $LiAlH_4$, THF: $TsOH \cdot H_2O$
step (iii) Br_2, CH_2Cl_2
step (iv) ^tBuOK, THF

Scheme 1. Synthetic route.

We describe as an example the synthesis of 4-[2-(*trans*-4-propylcyclohexyl)ethyl]-4′-ethyltolane ((I), $R^1 = C_3H_7$, $R^2 = C_2H_5$).

(i) To 9·2 g (0.07 M) of anyhydrous aluminium chloride in 50 cm³ of carbon disulphide, 10·6 g (0·06 M) of 4-ethylphenylacetyl chloride was added under cooling and 13·4 g of [2-(*trans*-4-propylcyclohexyl)ethyl]benzene, compound (*a*), was further added. The reaction mixture was stirred for 10 h at room temperature and treated with dilute hydrochloric acid. The product obtained was extracted with methylene chloride, washed and dried ($MgSO_4$). After removal of the solvent, the remaining solid was recrystallized from ethyl acetate to obtain 12·1 g of the ketone derivative of compound (*b*), m.p. 101·8°C.

(ii) This compound (*b*), 12·1 g, was dissolved in 25 cm³ of anhydrous tetrahydrofuran and treated with 0·9 g (0·025 M) of lithium aluminium hydride. The reaction mixture was treated with dilute sulphuric acid and the separated product was extracted with 20 cm^3 of toluene, washed and dried ($MgSO_4$). *p*-Toluenesulphonic acid 0·1 g was added, the mixture heated and the water produced was removed from the reaction system. Subsequently, the toluene phase was washed with water and dried ($MgSO_4$). After the toluene was evaporated, the residue was recrystallized from 30 cm^3 of ethyl acetate to obtain 8·5 g of compound (*c*), which showed liquid-crystalline phases (C–S; 143·9°C; S–N: 151·3°C. N–I: 197·9°C).

(iii) Compound (*c*) obtained in step (ii) was dissolved in 50 cm^3 of methylene chloride, to which 3·7 g of bromine was added at room temperature. The precipitate was collected by filtration and recrystallized from 40 cm^3 of *n*-heptane to obtain 7·4 g of a dibromoethane derivative (*d*), m.p. 204·5°C. This was dissolved in 40 cm^3 of anhydrous tetrahydrofuran and heated to 40°C with 7·4 g of potassium *t*-butoxide. After addition of 50 cm^3 of water, the resulting solid was extracted with methylene chloride and dried ($MgSO_4$). The product obtained was purified by column chromatography using a methylene chloride : *n*-hexane mixture (1 : 5 v/v) as eluant and silica gel as the stationary phase. A fraction of eluate showing a single spot with T.L.C. was collected and concentrated. The residue was recrystallized repeatedly from ethyl acetate to obtain a constant transition temperature. Through these steps mentioned, 4·8 g of 4-[2-(*trans*-4-propylcyclohexyl])ethyl]-4′-ethyltolane was obtained. (See table 1 for the transition temperature of this compound and other homologues prepared using this method.)

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