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Synthesis and Some Physical Properties of 1-Cyclohexyl-phenyl-2-Methyl Ethylenes

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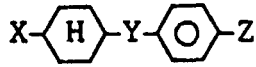
A series of trans-1-{4′-(trans-4″-*n*-alkylcyclohexyl)phenyl}-2-methylethylenes, which show nematic phases, were prepared. Their transition temperatures, enthalpies and entropies were measured. The phase diagrams for their binary mixtures were made and the birefringences and flow-aligned viscosities were measured. Five nematic mixtures were prepared to compare the properties of the ethylenes with those of other cyclohexylbenzenes having other terminal groups. The 1-cyclohexyl-phenyl-2-methylethylenes have wide nematic ranges with high N–I transition temperatures and high birefringences. Their photochemical stabilities were tested.

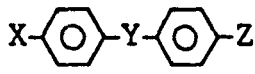
Keywords: liquid crystal, cyclohexane, ethylene, hydrocarbon

INTRODUCTION

Since the nematic cyclohexane carboxylates were reported in 1973,[1] nematic compounds containing a cyclohexyl ring have been synthesized.[2–5] The nematic compounds of formula (I), which have the same terminal groups (X, Z) and the same central group (Y) as the nematic compounds of formula (II) and replace the phenylene ring of formula (II) by a cyclohexyl ring, are low in viscosity and have broad mesomorphic ranges near room temperature. Replacement of the phenylene ring by a cyclohexyl ring reduces birefringence.



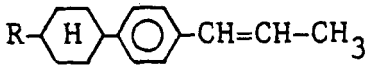
(I)



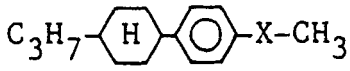
(II)

Some nematic hydrocarbons are low in viscosity at low temperature and suitable for automotive TN-display devices. We reported[6] that the phenyl cyclohexyl ethylenes have high birefringences and wide nematic ranges with high N–I transition temperatures.

To discuss the influence of the ethylenic group included in a terminal group on the properties of a nematic compound and to test the photochemical stability for the nematic hydrocarbon including a propenic group as the terminal group, we synthesized a new series of 1-cyclohexylphenyl-2-methylethylenes of formula (III) and compared the physical properties of compounds of formula (IV).



(III)



(IV)

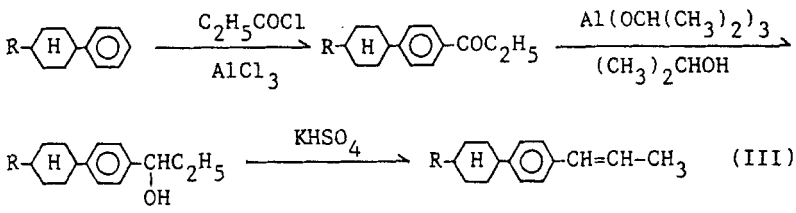
R= n-alkyl

X= -CH=CH-, -COO-,

$-OCH_2-$, $-CH_2CH_2-$

PREPARATION OF MATERIALS

The trans-1-{4′-(trans-4″-*n*-alkylcyclohexyl)phenyl}-2-methylethylenes were prepared according to the following scheme:



(III)

All of the products were distilled and purified by recrystallization from alcohol. The purity was tested by high pressure liquid chromatography and gas-liquid chromatography. Each product was identified by NMR spectrometry and mass spectrometry.

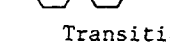
RESULTS AND DISCUSSION

The transition temperatures for the series of the trans-1-{4′-(trans-4″-*n*-alkylcyclohexyl)phenyl}-2-methylethylenes were measured by using a polarizing microscope equipped with a heating stage. The transition enthalpies (ΔH) were measured by differential scanning calorimetry and transition entropies (ΔS) were calculated from the transition enthalpies and the transition temperatures. These thermal data are listed in Table I. The transition temperatures and the transition entropies are plotted against the alkyl chain length in Figure 1 and Figure 2, respectively. The 1-(4′-cyclohexyl)phenyl-2-methylethylenes melt near room temperature and have broad nematic ranges. The nematic-to-isotropic (N–I) transition temperatures and N–I transition entropies exhibit odd-even effects, the odd chain lengths being associated with the higher values. The crystal-to-nematic (C–N) transition temperatures of the homologous series remain nearly constant around 30°C. The C–N transition entropy for alkyl chain length 5 becomes larger.

The phase diagram and the birefringences (Δn) for the binary mixtures of the trans-1-{4′-(trans-4″-ethylcyclohexyl)phenyl}-2-methylethylene (V) and the trans-1-{4′-(trans-4″-*n*-propyl-cyclohexyl)phenyl}-2-methylethylene (VI) are shown in Figure 3. The binary mixture consisting of 53% of compound (V) and 47% of compound (VI) is an eutectic mixture. Birefringences were measured at 25°C

TABLE I

Transition temperatures, enthalpies (ΔH) and entropies (ΔS) for the trans-1-{4′-(trans-4″-*n*-alkylcyclohexyl)phenyl}-2-methylethylenes



Compound	R	Transition temp. (°C)		ΔH (kcal/mol)		ΔS (EU)	
		C–N	N–I	C–N	N–I	C–N	N–I
(V)	C_2H_5–	34	51	3.66	0.112	11.9	0.346
(VI)	C_3H_7–	37	85	3.80	0.174	12.3	0.486
(VII)	C_4H_9–	34	78	2.95	0.115	9.6	0.328
(VIII)	C_5H_{11}–	27	92	5.95	0.167	19.7	0.458

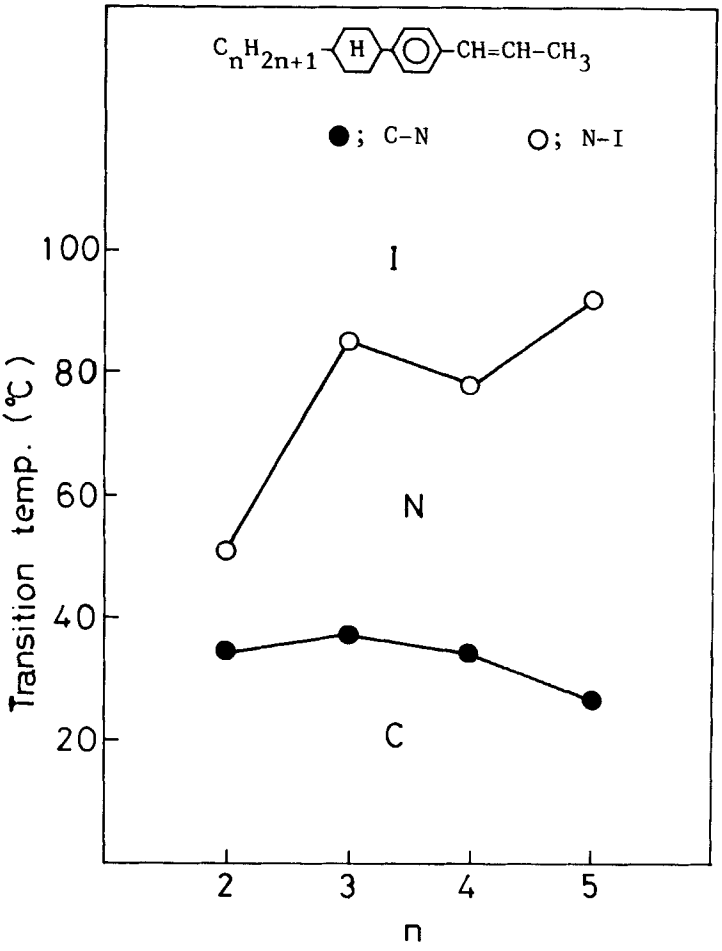


FIGURE 1 Plot of phase transitions against alkyl chain length (n) for the trans-1-{4′-(trans-4″-n-alkylcyclohexyl)phenyl}-2-methylethylenes.

by polarizing microscopy using a compensator. The birefringences of compound (V) and compound (VI) are determined by extrapolation in Figure 3. The birefringences for the homologous series of alkyl chain length 4 and 5 are obtained similarly. These birefringences are plotted against the alkyl chain length in Figure 4. The birefringences show an odd-even effect, the odd chain lengths being associated with the higher values. The viscosity for the binary mixture of 20% of compound (V) and 80% of compound (VI) is 8.6 c.p. at 20°C. It is extremely low compared with other nematic mixtures.

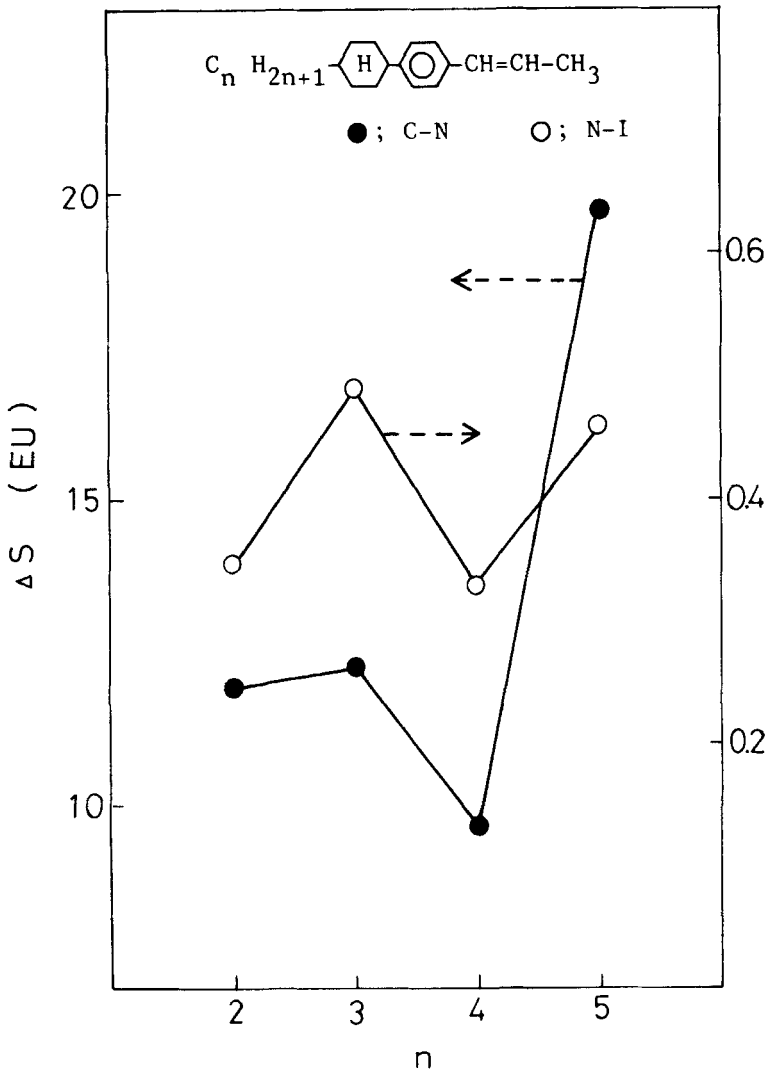


FIGURE 2 Transition entropy vs. alkyl chain length (n) for the trans-1-{4′-(trans-4″-n-alkylcyclohexyl)phenyl}-2-methylethylenes.

The transition temperatures against the different X in formula (IV) are plotted in Figure 5. The compounds of X = —COO— and X = —OCH_2— show monotropic nematic phases. As the compound of X = —CH_2CH_2— does not show a nematic phase, the virtual N–I transition temperature is determined by extrapolation. Figure 5 shows that the compound of X = —CH=CH— has a higher N–I

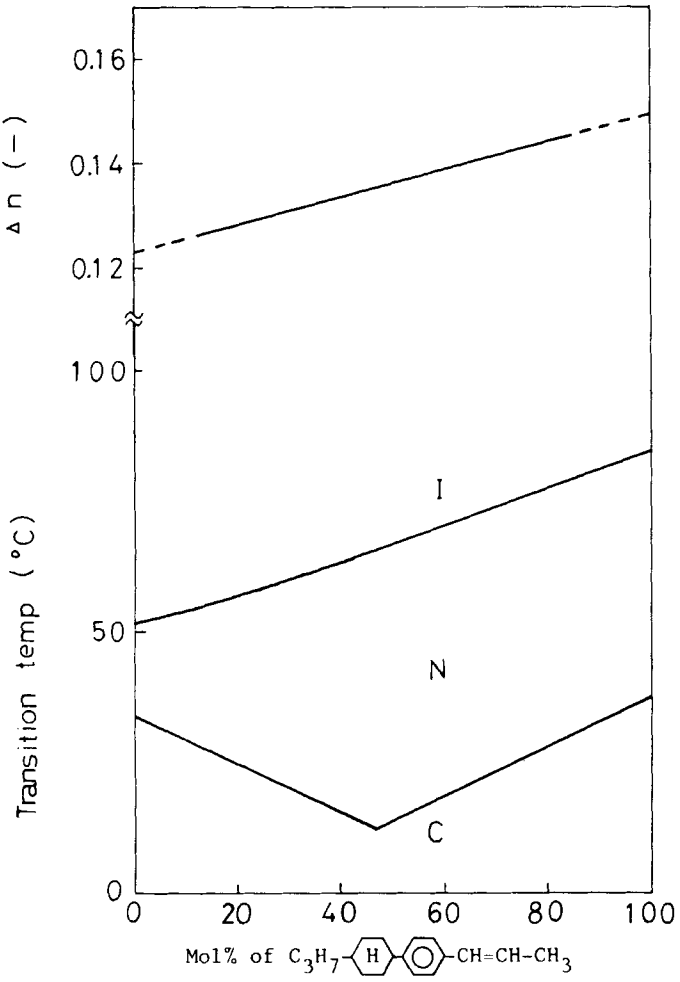
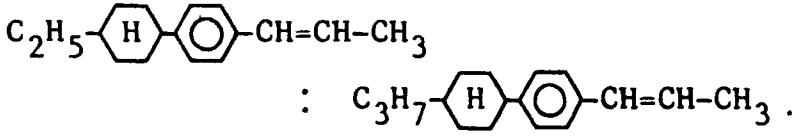


FIGURE 3 Phase diagram and birefringences for



transition temperature and a broad nematic range. The ethylenic group included in the terminal group for the trans-1-{4′-(trans-4″-*n*-propylcyclohexyl)phenyl}-2-methylethylene has enhanced the N–I transition temperature and widened the nematic range the same as

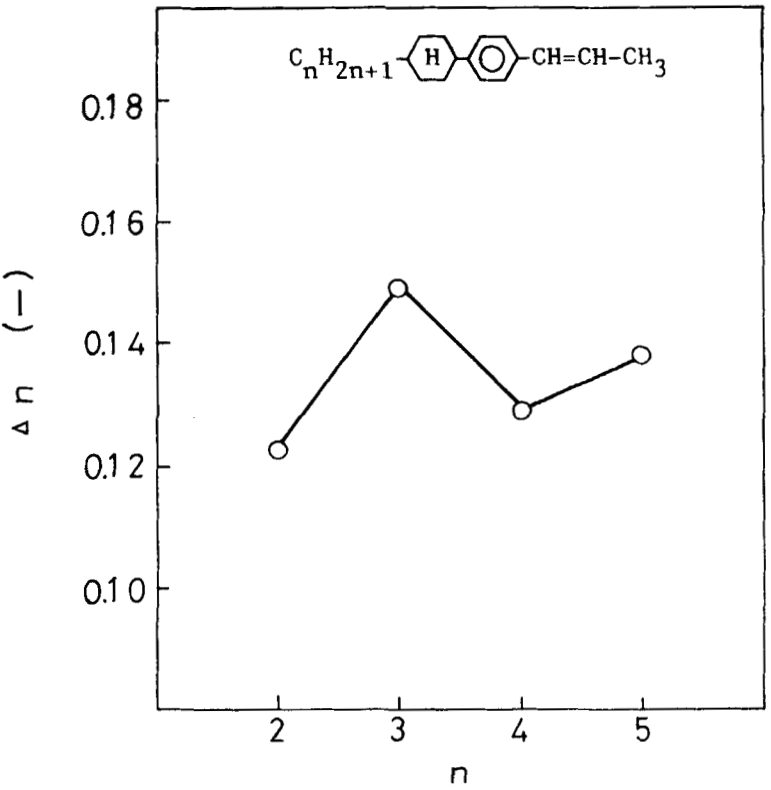


FIGURE 4 Birefringence vs. alkyl chain length (n) for the trans-1-{4′-(trans-4″-n-alkylcyclohexyl)phenyl}-2-methylethylenes.

one for a central group for the trans-1-(4′-substituted phenyl)-2-(trans-4″-n-alkylcyclohexyl)ethylenes.[6]

In order to discuss the influence of X in formula (IV), mixture (A) and the following nematic mixtures of mixture (A) and four kinds of compounds of formula (IV) were prepared:

1: mixture (A)

75 % of mixture (A) + 25 % of C_3H_7-H-X-CH_3

2: X= -CH=CH-

3: X= -COO-

4: X= $-OCH_2-$

5: X= $-CH_2CH_2-$

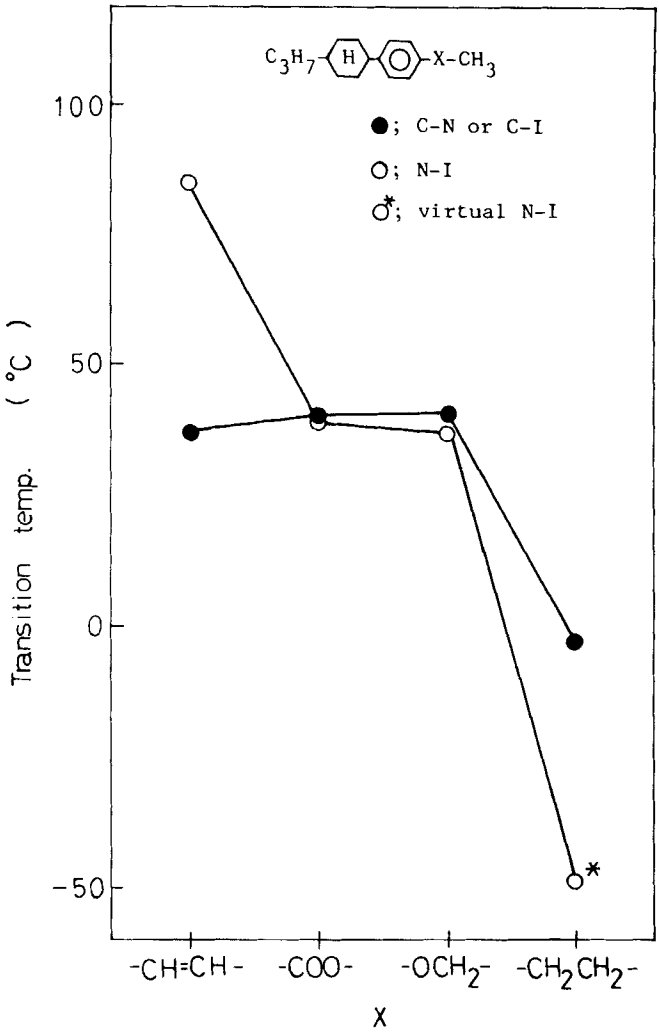


FIGURE 5 Transition temperatures of the nematic compounds having different X in formula (IV).

The composition and physical properties of mixture (A) are as follows:

Composition: 40 wt% of C_3H_7-H-CN

30 wt% of C_5H_{11}-H-CN

30 wt% of C_7H_{15}-(H)-(O)-CN

N-I transition temperature:	51.0 °C
Flow-aligned viscosity at 20°C:	21.4 c.p.
Birefringence at 25°C:	0.118

The temperature dependence of the flow-aligned viscosities for these five nematic mixtures is shown in Figure 6. Nematic mixture 2 (X = —COO—) and nematic mixture 3 (X = —CH=CH—) have

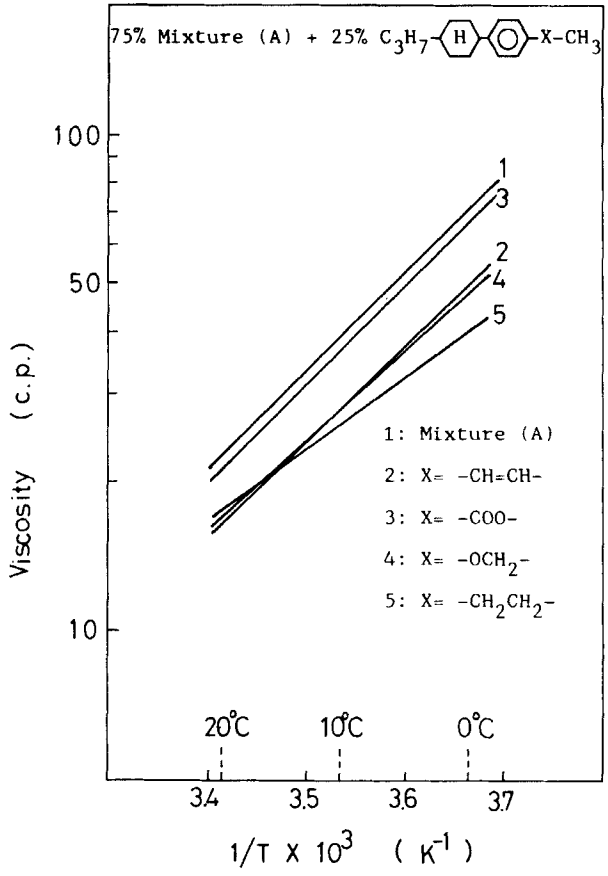


FIGURE 6 Temperature dependence of flow-aligned viscosities for mixture (A)—(see text) and 75% of mixture (A) + 25% of C_3H_7-(H)-(O)-X-CH_3.

a similar activation energy to that of mixture (A). The activation energy for nematic mixture 4 (X = —OCH_2—) is slightly smaller than these and that for nematic mixture 5 (X = —CH_2CH_2—) is the smallest. They can be attributed to a decrease of polarities of nematic mixture 4 and nematic mixture 5.

The flow-aligned viscosity at 0°C of each compound (IV) was determined by extrapolation and is shown in Figure 7. The order of the flow-aligned viscosity at 0°C is the following:

$$-COO- \gg -CH{=}CH- > -OCH_2- > -CH_2CH_2-$$

The viscosity of the compound of X = —CH=CH— is 17 c.p. at 0°C, which is slightly lower than that of X = —OCH_2— and re-

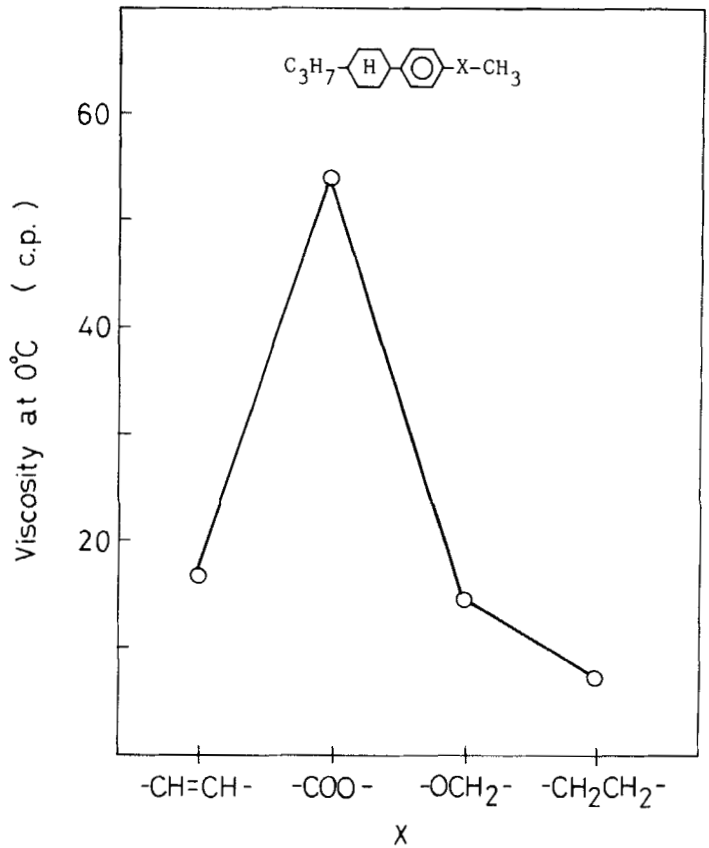


FIGURE 7 Flow-aligned viscosities at 0°C of the nematic compounds having different X in formula (IV).

markably lower than that of X = —COO—. The order of viscosity at 0°C (nematic mixture 2 > 4 > 5) is reversed at 20°C (nematic mixture 5 > 4 > 2). It can be attributed to low N–I transition temperatures of nematic mixture 4 (43.0°C) and nematic mixture 5 (26.0°C).

The birefringences at 25°C of the compounds of X = —COO— and X = —OCH_2— were determined by extrapolation and are compared with that of X = —CH=CH— in Figure 8. The birefringence of the compound of X = —CH_2CH_2— was not determined by extrapolation because of a decrease of the N–I transition temperature.

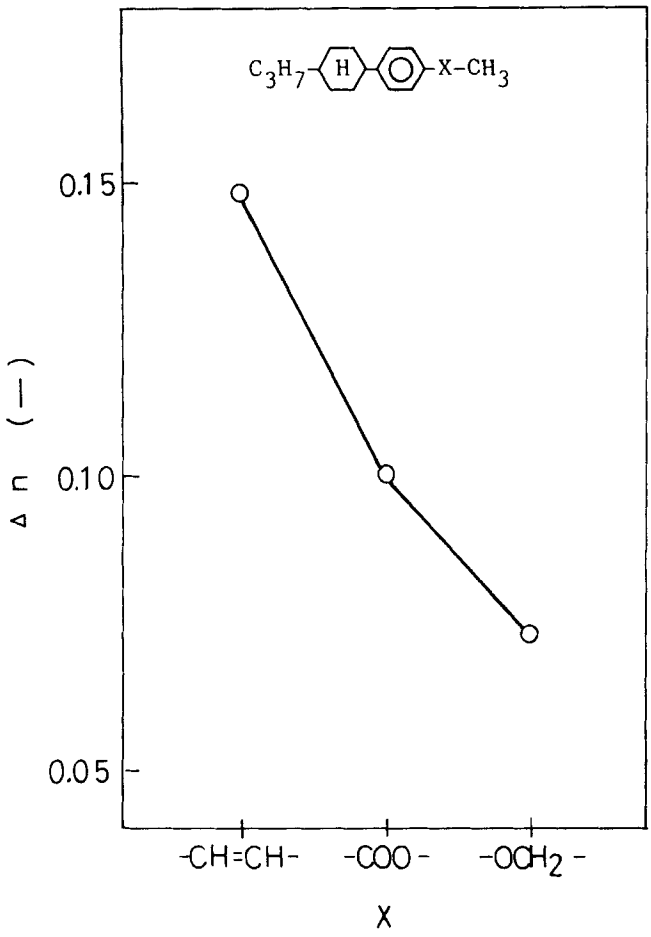
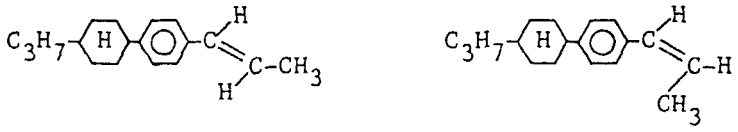


FIGURE 8 Birefringences (Δn) of the nematic compounds having different X in formula (IV).

Figure 8 shows that the ethylenic group (—CH=CH—) included in a terminal group enhances the birefringence the same as that[6] for a central group.

The trans-ethylene is isomerized to the cis-ethylene by UV irradiation. Isomerization for the 1-cyclohexylphenyl-2-methylethylene involves the following geometric change:



The photochemical stability of the trans-1-cyclohexylphenyl-2-methylethylene can be tested by checking the N–I transition temperature depression because the production of the cis-ethylene remarkably reduces the N–I transition temperature.

The N–I transition temperatures for compound (VI) protected with no filter (1) and with a Fuji filter SC-41 (2) were measured after UV exposure by a SUNTEST (ORIGINAL HANAU). The technical and light data of the SUNTEST are shown in a previous paper.[6] The N–I

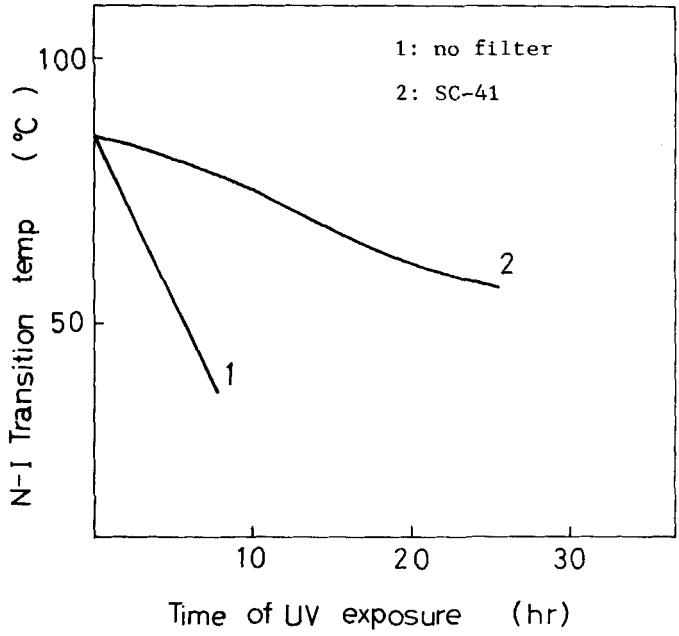


FIGURE 9 N–I transition temperature vs. time of UV exposure for trans-1-{4'-(trans-4''-*n*-propylcyclohexyl)phenyl}-2-methylethylene.

transition temperature vs. time of UV exposure for compound (VI) is shown in Figure 9. The Fuji filter SC-41 absorbs light of wavelengths shorter than 410 nm. The N–I transition temperatures of compound (VI) both with a Fuji filter SC-41 and with no filter are decreased remarkably by UV irradiation.

Total conversions (a) and yields of the cis-ethylene (b) after UV irradiation were measured by gas-liquid chromatography and are shown in Figure 10. The cis-ethylene produced after UV irradiation is identified by the fact that it has the same mass spectrum as compound (VI).

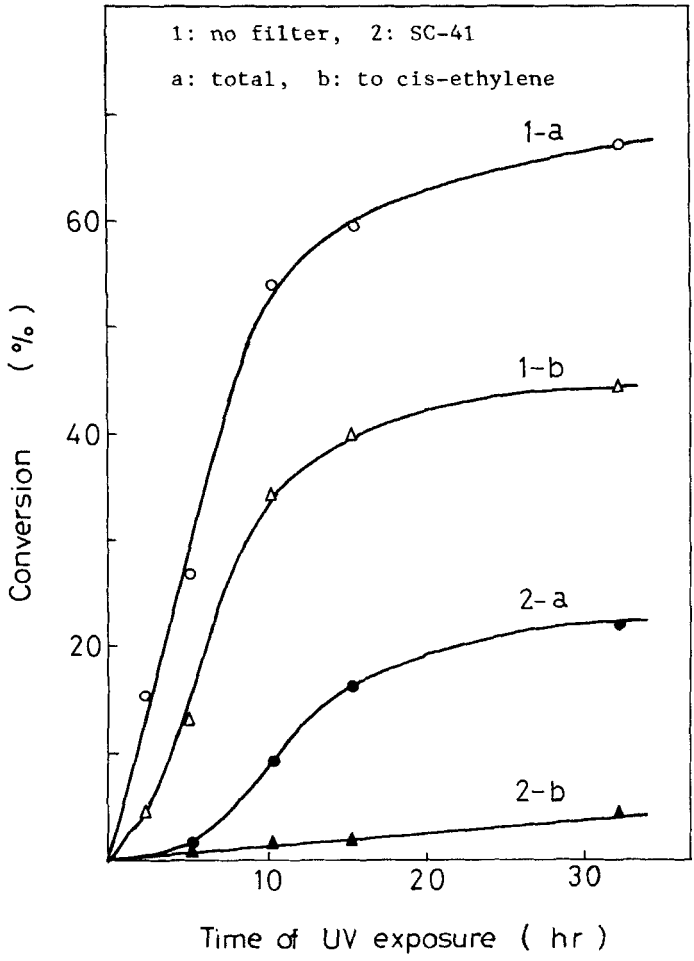


FIGURE 10 Conversion vs. time of UV exposure for trans-1-{4′-(trans-4″-*n*-propylcyclohexyl)phenyl}-2-methylethylenes.

The mass spectrum was recorded on GCMS-QP1000. The yield of the cis-ethylene protected with a Fuji filter SC-41 (2-b) is kept down to about 4% after UV exposure for 30 hours. The total conversion (2-a), however, reaches 20% because the other unknown products are yielded. The value of {(1-a)−(1-b)} is nearly equal to the value of {(2-a)−(2-b)} in Figure 10. Conversion to other products except the cis-ethylene is not kept down by cutting the light of wavelengths shorter than 410 nm.

Acknowledgment

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