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Synthesis and Some Physical Properties of Phenyl Cyclohxyl Ethylenes

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Synthesis and Some Physical Properties of Phenyl Cyclohexyl Ethylenes

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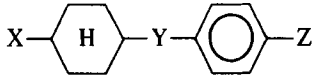
(Received July 23, 1982; in final form November 22, 1982)

Some series of trans-1-(4-substituted phenyl)-2-(trans-4-*n*-alkylcyclohexyl) ethylenes, which show nematic phases, were prepared. Their transition temperatures, birefringences and bulk viscosities were measured. Their properties are compared with those of other nematic cyclohexanes: phenyl cyclohexane carboxylates, phenyl thiol cyclohexane carboxylates and phenyl cyclohexanes. The phenyl cyclohexyl ethylenes have wide nematic ranges with high clearing points and have high birefringences. Their photochemical stabilities were tested.

INTRODUCTION

Since Demus *et al*[1] reported the nematic cyclohexane carboxylates in 1973, several kinds of nematic compounds (I) containing a cyclohexyl ring have been synthesized.[2–5]

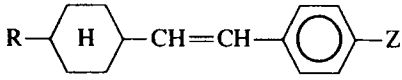


(I)

Their nematic phases, which are low in viscosity and have mesomorphic ranges near room temperature, are suitable for TN-display devices. Replacement of a phenylene ring by a cyclohexyl ring reduces birefringence; this can be confirmed by comparing the values for the compounds (I) with those for the corresponding compounds having two phenylene rings: phenyl benzoates,[6,7] cyanobiphenyls,[8] and phenyl thiol benzoates.[9,10] High birefringence is, however, required for most of TN-display devices.

To achieve the compounds of type (I) of high birefringence and high clearing temperature, we selected the ethylenic group (—CH=CH—) as

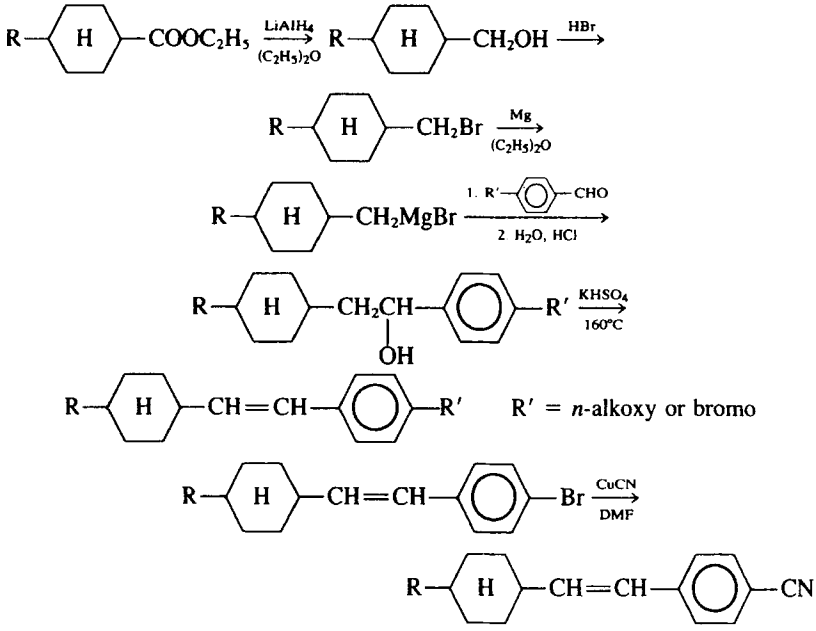
Y in formula (I) and synthesized new series of phenyl cyclohexyl ethylenes; their general formula is:



R = *n*-alkyl
Z = *n*-alkoxy or cyano

PREPARATION OF MATERIALS

The phenyl cyclohexyl ethylenes were prepared according to the following scheme:



All of the products were distilled and purified by recrystallization from *n*-hexane/alcohol. The purity was tested by high pressure liquid chromatography and gas-liquid chromatography. Each product was identified by NMR spectrometry and mass spectrometry. The NMR data of the trans-1-(4-methoxyphenyl)-2-(trans-4-*n*-propylcyclohexyl) ethylene are shown in Table I. It was confirmed from J values of H_a and H_b that the pure trans-ethylene contained no cis-isomer.

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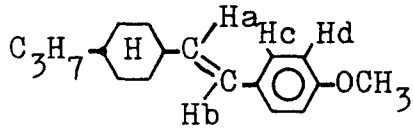
TABLE I

NMR of the trans-1-(4-methoxyphenyl)-2-(trans-4-*n*-propylcyclohexyl)ethylene



	δ(ppm)			
CH_3-C-	0.88	t	3	
-C-CH_2-C	0.9 ~ 1.4	m	4	
-⟨H⟩-	1.0 ~ 2.2	m	10	
-O-CH_3	3.78	s	3	
Ha	6.0	d,d	1	J = 11Hz, 4Hz
Hb	6.3	d	1	J = 11Hz
Hd	6.81	d	2	J = 6Hz
Hc	7.26	d	2	J = 6Hz

RESULTS AND DISCUSSION

1 Mesomorphic properties

The transition temperatures for the series of the trans-1-(4-*n*-alkoxyphenyl)-2-(trans-4-*n*-alkylcyclohexyl) ethylenes and the trans-1-(4-cyanophenyl)-2-(trans-4-*n*-alkylcyclohexyl) ethylenes were measured by using a polarizing microscope equipped with a heating stage and are listed in Table II. The mesomorphic properties of the phenyl cyclohexyl ethylenes are characterized by high clearing points and wide nematic ranges. The phenyl cyclohexyl ethylenes have clearing points of about 100°C; amongst the highest for nematic compounds containing two ring systems.

In Figure 1 and Figure 2, these transition temperatures are compared with those of nematic compounds having different central groups Y (—COO—, —COS—, —) and the same terminal groups X, Z in formula (I). For the ethoxy derivatives in Figure 1, all the clearing points of the four series exhibit the same trends as a function of the number of carbon atoms in the alkyl chain:

$$n = 5 > n = 3 > n = 4$$

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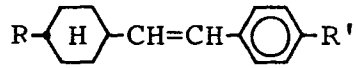
TABLE II

Transition temperatures (°C) of trans-1-(4-substituted phenyl)-2-(trans-4-*n*-alkylcyclohexyl)ethylenes



R	R′	m.p.	clp.
C_2H_5-	-OCH_3	44	61
C_2H_5-	-OC_2H_5	49	73
n-C_3H_7-	-OCH_3	34	92
n-C_3H_7-	-OC_2H_5	79	106
n-C_3H_7-	-OC_4H_9	38	98
n-C_4H_9-	-OC_2H_5	44	101
n-C_5H_{11}-	-OCH_3	49	97
n-C_5H_{11}-	-OC_2H_5	64	109
C_2H_5-	-CN	66	71
n-C_3H_7-	-CN	63	105
n-C_4H_9-	-CN	57	98
n-C_5H_{11}-	-CN	50	97

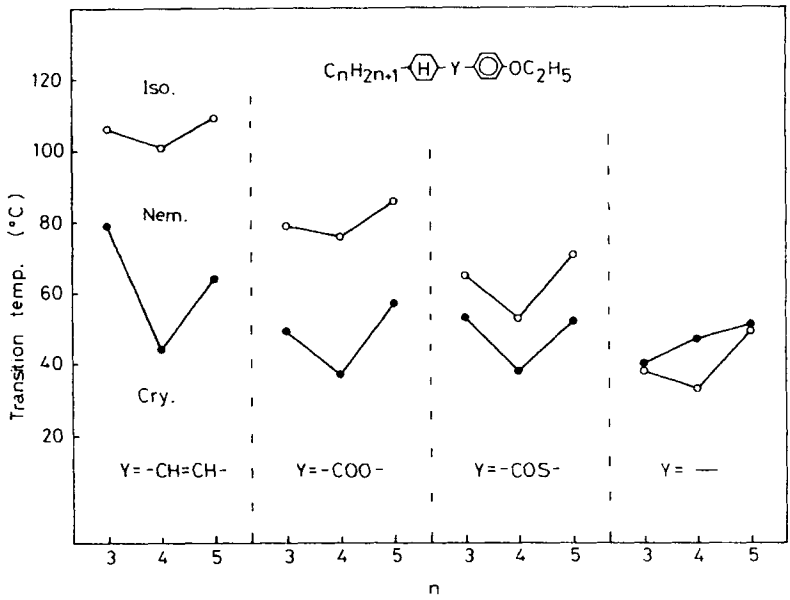


FIGURE 1 Comparison of the transition temperatures for ethoxy phenyl cyclohexyl ethylenes and other corresponding nematic cyclohexanes.

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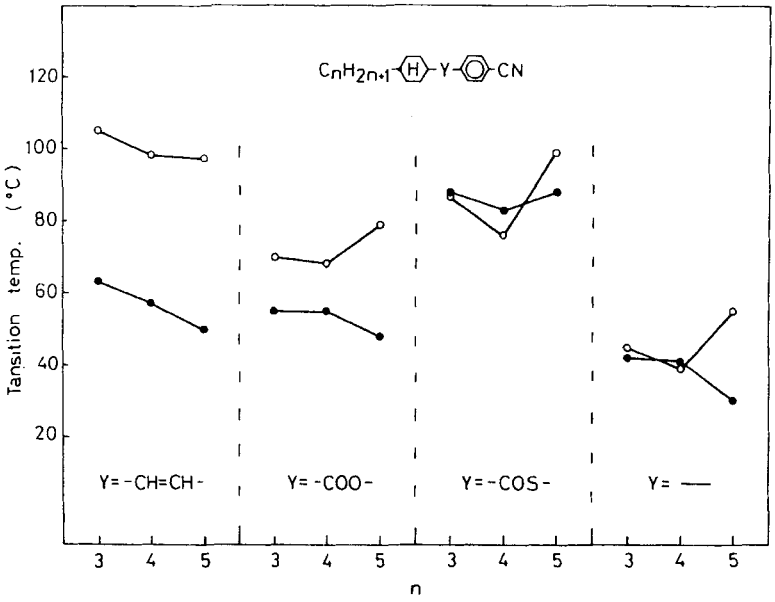

FIGURE 2 Comparison of the transition temperatures for cyano phenyl cyclohexyl ethylenes and other corresponding nematic cyclohexanes.

The orders of the clearing points and the nematic ranges for the nematic compounds with different central groups Y are as follows:

clearing points

$$-CH{=}CH- > -COO- > -COS- > -$$

nematic ranges

$$-CH{=}CH- > -COO- > -COS- > -$$

As shown in Figure 2, the orders of the clearing points and nematic ranges for the cyano derivatives are as follows:

clearing points

$$-CH{=}CH- > -COS- > -COO- > -$$

nematic ranges

$$-CH{=}CH- > -COO- > -COS-, -$$

Both the ethoxy and cyano derivatives of the phenyl cyclohexyl ethylenes have wider nematic ranges with higher clearing points than the correspond-

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ings of cyclohexane carboxylates, thiol cyclohexane carboxylates and phenyl cyclohexanes. The ethylenic group has enhanced the clearing points and widened the nematic ranges as a linkage between a cyclohexyl ring and a phenylene ring in comparison with other groups.

2 Birefringence

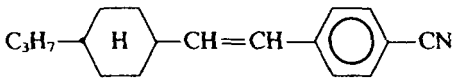
Birefringences were measured by polarizing microscopy using compensator.

In Table III, birefringence data (Δn) for compounds (II), (III), (IV) and (V) are depicted.

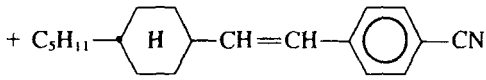
The birefringences of compounds (II) and (IV) were measured in the supercooled states. As compound (III) and compound (V) do not exhibit nematic phases at 25°C, their birefringences were determined by extrapolation from data obtained from a series of solutions of the compound in a mixture of cyclohexane carboxylates as shown in Figure 3. The birefringences are compared with that of the 4-*n*-pentyl-4′-cyanobiphenyl (K-15), which is a popular compound having a high birefringence. Compound (III) has a higher birefringence than K-15. Birefringence decreases rapidly with increasing alkyl chain length from 3 to 5.

To assess the effect of the different central groups Y on birefringence, the following three nematic mixtures were prepared:

DCE mixture

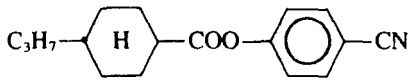


(50 wt%)

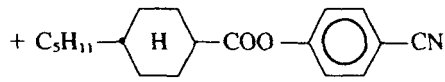


(50 wt%)

ECH mixture



(50 wt%)



(50 wt%)

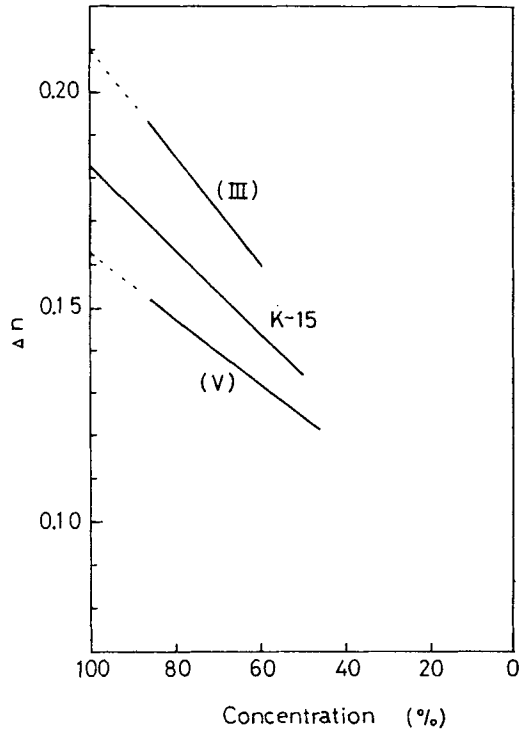
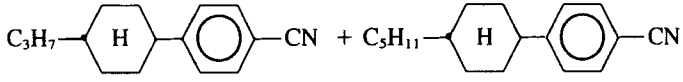


FIGURE 3 Birefringence (Δn) vs. concentration of trans-1-(4-cyano phenyl)-2-(trans-4-*n*-propylcyclohexyl) ethylene (III), trans-1-(4-cyanophenyl)-2-(trans-4-*n*-pentylcyclohexyl)-ethylene (V) and 4-*n*-pentyl-4′-cyano biphenyl (K-15) in 4-*n*-alkoxyphenyl 4′-*n*-alkylcyclohexane-1-carboxylates. λ : 526 nm.

PCH mixture



(50 wt%) (50 wt%)

The temperature dependence for the DCE mixture, the ECH mixture and the PCH mixture is shown in Figure 4. The three mixtures can be considered to have the same alkyl chain length. The birefringence of the DCE mixture is obviously higher than that of the PCH mixture or the ECH mixture. The ethylenic group effectively raises the birefringence as a central group Y in formula (I).

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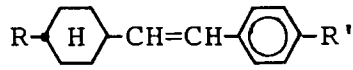
TABLE III

Birefringences (Δn) of trans-1-(4-substituted phenyl)-2-(trans-4-*n*-alkylcyclohexyl)ethylenes



R	R'	Compound No.	Δn (25°C, 526 nm)
n-C_3H_7-	-OCH_3	(II)	0.145*
n-C_3H_7-	-CN	(III)	0.210**
n-C_4H_9-	-CN	(IV)	0.180*
n-C_5H_{11}-	-CN	(V)	0.163**

measured *in the supercooled state
**by extrapolation

3 Bulk viscosity

The viscosity measurements in the nematic ranges were made using a rotating cone-plate viscometer. Figure 5 shows the dependence of the bulk viscosity for the DCE mixture, the ECH mixture, the PCH mixture and compound (II). The order of bulk viscosity for the three mixtures having different central groups and the same terminal groups is the following:

DCE mixture > ECH mixture > PCH mixture

(—CH=CH—) (—COO—) (—)

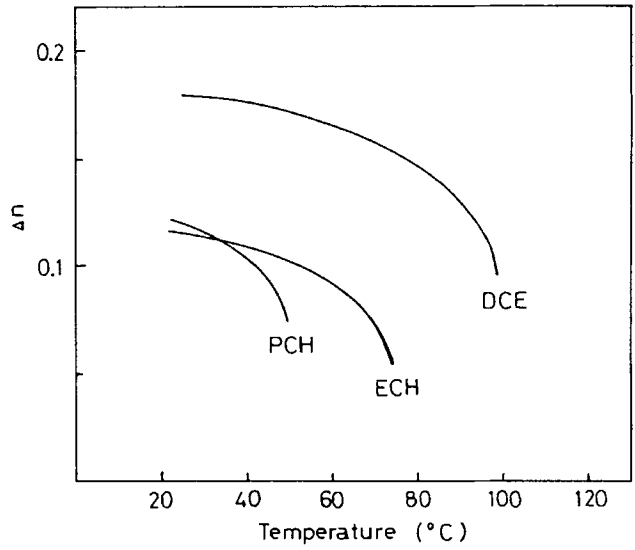


FIGURE 4 Temperature dependence of the birefringence for cyanophenyl cyclohexyl ethylenes (DCE), cyanophenyl cyclohexane carboxylates (ECH) and cyanophenyl cyclohexanes (PCH). λ : 526 nm.

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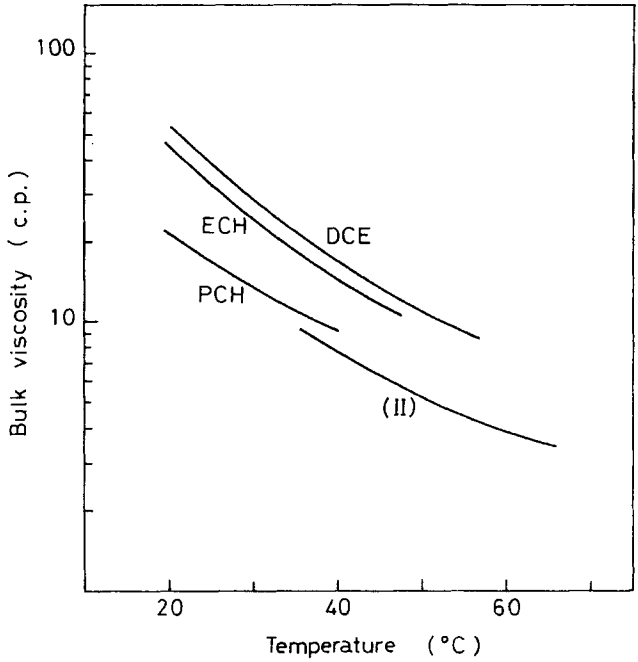
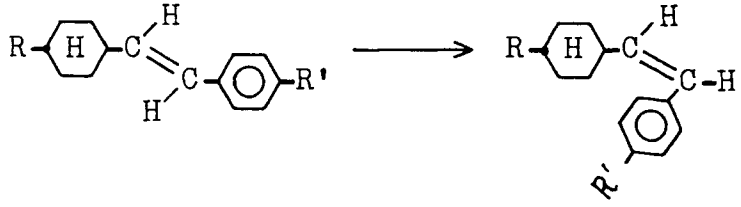


FIGURE 5 Temperature dependence of the bulk viscosity for cyanophenyl cyclohexyl ethylenes (DCE), cyanophenyl cyclohexane carboxylates (ECH), cyanophenyl cyclohexanes (PCH) and trans-1-(4-methoxyphenyl)-2-(trans-4-*n*-propylcyclohexyl)-ethylene (II).

The phenyl cyclohexyl ethylene system has a similar activation energy to that of the cyclohexane carboxylate and is slightly more viscous. The viscosity of compound (II), which has a wide nematic range (34 ~ 92°C), is very low (7.6 c.p. at 40°C) because of the short alkyl and alkoxy chains. It is lower than that of the PCH mixture which involves no central groups.

4 Photochemical stability

The trans-ethylene is isomerized to the cis-ethylene by UV irradiation. Isomerization for the phenyl cyclohexyl ethylene involves the following geometric change:



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As the cis-ethylenes generally exhibit no mesophases, the clearing points for the trans-1-phenyl-2-cyclohexyl ethylenes must be decreased on isomerization. Therefore, the photochemical stability of the trans-1-phenyl-2-cyclohexyl ethylenes can be tested by checking the clearing point depression.

The new product after UV irradiation for compound (II) is to be cis-1-(4-methoxyphenyl)-2-(trans-4-*n*-propylcyclohexyl) ethylene because it has the same mass spectrum as compound (II). The concentration of the cis-isomer was measured by gas-liquid chromatography (Silicone SE-52) and the mass spectrum was recorded on a GCMS-QP1000. The clearing point for compound (II) as a function of concentration of cis-isomer is shown in Figure 6. The clearing point for compound (II) decreases by 10°C when only 2% of cis-isomer is produced.

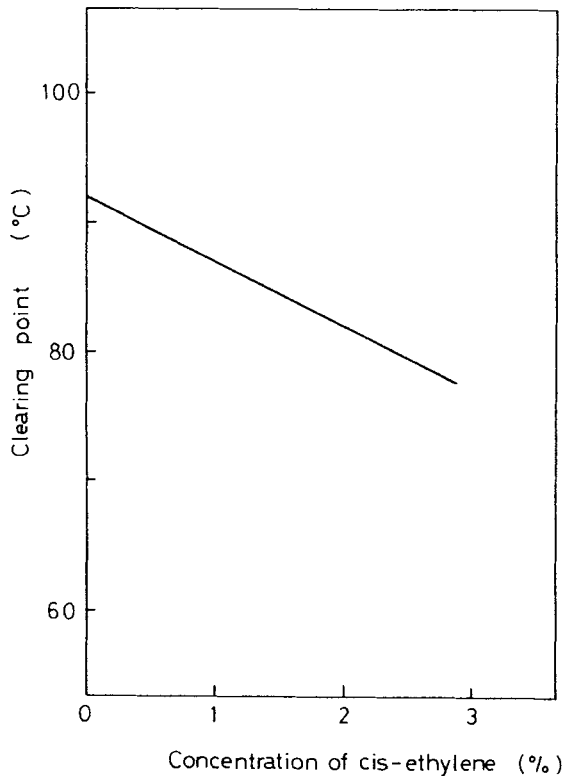

FIGURE 6 Clearing point *vs* concentration of cis-ethylene for 1-(4-methoxyphenyl)-2-(trans-4-*n*-propylcyclohexyl) ethylene.

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The clearing points for compound (II) protected with different kinds of filter, or with no filter were measured after UV exposure by a SUNTEST (ORIGINAL HANAU). The technical and light data of the SUNTEST are as follows:

Xennon burner rating:	1.1 kw
Temperature at specimen level:	60°C
Distance from burner axis to specimen surface:	230 mm
Light intensity:	150 klx
Radiation intensity between 300 and 830 nm:	830 W/m^2

The clearing point *vs* time of UV exposure for compound (II) is shown in Figure 7.

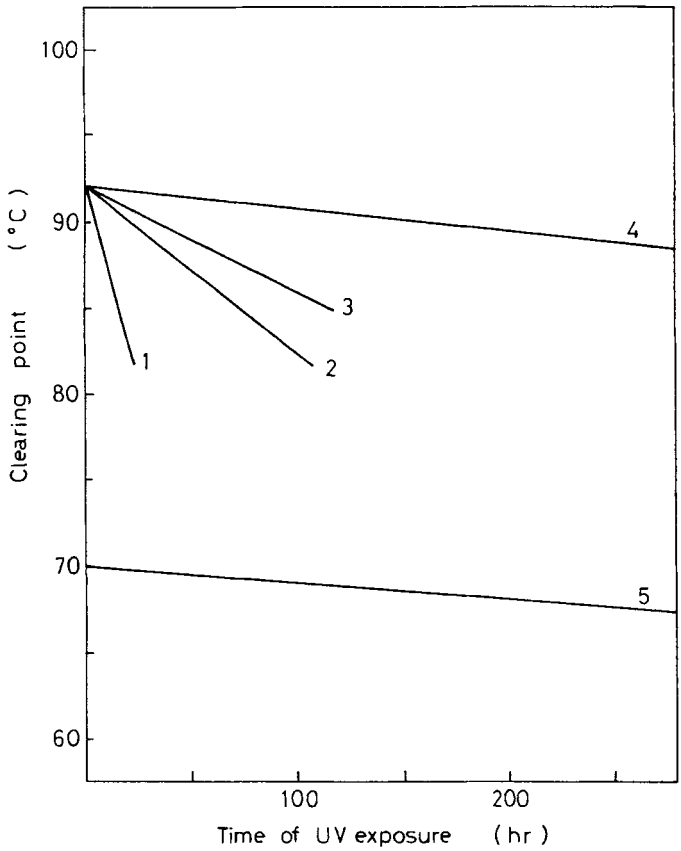

FIGURE 7 Clearing point *vs* time of UV exposure for trans-1-(4-methoxyphenyl)-2-(trans-4-n-propylcyclohexyl)ethylene (1 : no filter, 2 : SC-41, 3 : SC-42, 4 : SC-48) and NP-1132 with SC-41 (5).

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Fuji filters SC-41, SC-42 and SC-48 absorb light of shorter wavelength than 410 nm, 420 nm and 480 nm respectively. NP-1132 is a commercial liquid crystal mixture of phenyl cyclohexanes and a biphenylcyclohexane. The clearing point depression by UV exposure for compound (II) protected with Fuji filter SC-48 is similar to that for NP-1132 protected with Fuji filter SC-41.

Acknowledgment

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