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Synthesis and Some Properties of Nematic Compounds Containing Three Ring Systems

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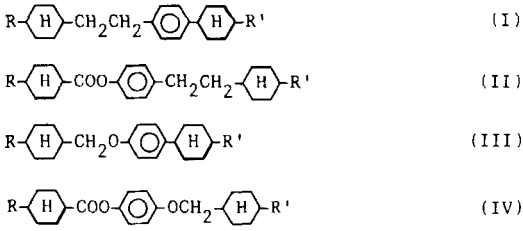
Four series of nematic compounds: 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes, 4-{β-(*trans*-4′-*n*-alkylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates, *trans*-4-*n*-alkylcyclohexylmethyl 4′-(*trans*-4″-*n*-alkylcyclohexyl)phenyl ethers and 4-(*trans*-4′-*n*-alkylcyclohexyl)methoxyphenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates, were prepared and their transition temperatures and transition entropies measured. Their flow-aligned viscosities and birefringences were determined by extrapolation. The N–I transition temperatures and entropies for the 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes and 4-{β-(*trans*-4′-*n*-propylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates exhibit odd-even effects in relation to the number of carbon atoms in the alkyl chain. The viscosity of 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-propylcyclohexyl)phenyl}ethane is 17.0 c.p. at 20 °C and the viscosity of 4-{β-(*trans*-4′-*n*-propylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-propylcyclohexane-1″-carboxylate is 34.0 c.p. at 20°C.

INTRODUCTION

Nematic compounds of low viscosity with a high clearing point are required in order to achieve TN-display devices having short response times and to be driven at higher temperatures. Nematic cyclohexane carboxylates,[1] which are low in viscosity and have broad nematic ranges with high clearing points, are suitable for high level multiplexing.[2] Gray *et al.*[3] presented nematic compounds containing the ethylene (CH_2CH_2) linkage between a phenylene and a cyclohexyl ring. The ethylene linkage maintains the linearity of the nematic molecule

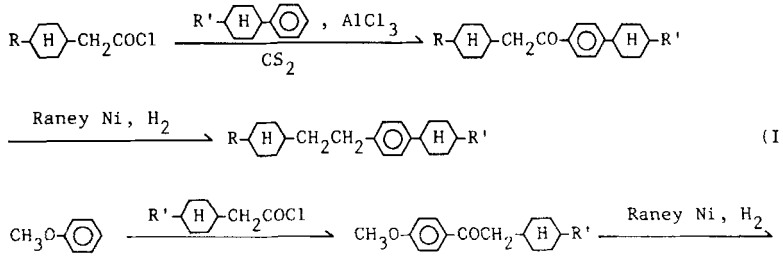
and has flexibility. Some nematic hydrocarbons[4] containing three or four ring systems, which have low viscosity coupled with high clearing points, are also very useful for automobile display device applications.

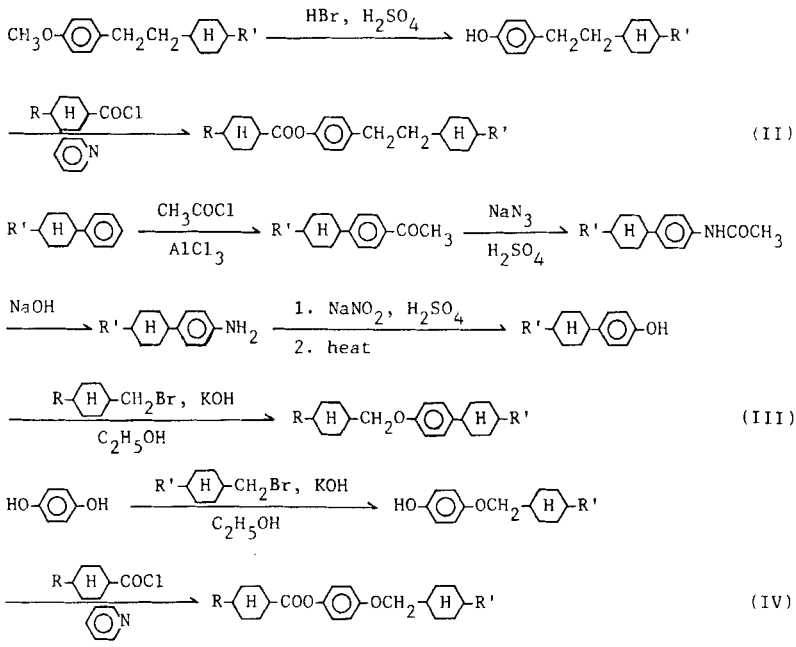
We have synthesized a series of 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes of formula (I) and a series of 4-{*β*-(*trans*-4′-*n*-alkylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexyl-1″-carboxylates of formula (II) in order to achieve a nematic compound of low viscosity with a high clearing point, and have prepared nematic compounds of formula (III) and (IV) in order to investigate the effect of the ethylene linkage between a cyclohexyl and a phenylene ring on mesomorphic and physical properties compared with that of other linkages.



PREPARATION OF MATERIALS

The 1-(*trans*-4′-*n*-alkylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes (I), the 4-{*β*-(*trans*-4′-*n*-alkylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates (II), the *trans*-4-*n*-alkylcyclohexylmethyl 4′-(*trans*-4″-*n*-alkylcyclohexyl)phenyl ethers (III) and the 4-(*trans*-4′-*n*-alkylcyclohexyl)methoxyphenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates (IV) were prepared according to the following scheme:





(II)

(III)

(IV)

The *trans*-4-*n*-alkylcyclohexylacetyl chloride was prepared from *trans*-4-*n*-alkylcyclohexylmethyl magnesium bromide and carbon dioxide in absolute ether, followed by interaction with thionyl chloride. Each compound was purified by chromatography on silica gel, eluting with a mixture of hexane and benzene, followed by recrystallization from hexane/alcohol. The structures were confirmed by NMR spectrometry and mass spectrometry. The purity was tested by high pressure liquid chromatography and gas-liquid chromatography.

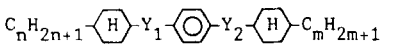
RESULTS AND DISCUSSION

The transition temperatures for the four series of nematic compounds were measured by using a polarizing microscope equipped with a heating stage. The transition enthalpies (ΔH) were measured by differential scanning calorimetry and the transition entropies (ΔS) were calculated from the transition enthalpies and the transition temperatures. The transition temperatures are listed in Table I.

The plot of the phase transitions against the alkyl chain length for the 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes is shown in Figure 1. The nematic to isotropic

TABLE I

Transition temperatures for four series of nematic compounds containing three ring systems—a phenylene and two cyclohexyl rings



Series	Y_1	Y_2	n	m	Transition temp. (°C) C	S	N	I
			2	3	· 71	· 81	· 103	·
			3	2	· 58	· 78	· 105	·
(I)	CH_2CH_2	—	3	3	· 46	· 106	· 131	·
			3	4	· 35	· 117	· 126	·
			3	5	· 26	· 131	· 134	·
			2	3	· 80	· —	· 145	·
(II)	COO	CH_2CH_2	3	3	· 102	· —	· 163	·
			4	3	· 100	· 110	· 160	·
			5	3	· 68	· 122	· 163	·
(III)	CH_2O	—	3	2	· 84	· 91	120	
			3	3	· 67	· 98	140	
			3	2	· 97	· —	· 146	·
(IV)	COO	OCH_2	3	3	· 115	· —	· 169	·
			5	2	· 85	· —	· 145	·
			5	3	· 102	· —	· 169	·

(N–I) transition temperatures exhibit an odd-even effect, the odd chain lengths being associated with the higher values. The smectic to nematic (S–N) transition temperatures increase with increase in alkyl chain length, whereas the crystal to smectic (C–S) transition temperatures decrease. The temperature ranges of the smectic phases become broad with increase in alkyl chain length. The N–I and S–N transition entropies for the 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes are plotted against the alkyl chain length in Figure 2. The N–I and S–N transition entropies show an odd-even effect, the odd chain lengths being associated with the higher values as for the N–I transition temperatures.

The plot of the phase transitions against the alkyl chain length for the 4-{β-(*trans*-4′-*n*-propylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates is shown in Figure 3. The N–I transition temperatures again exhibit an odd-even effect. Smectic phases appear from an alkyl chain length of four. The N–I and the C–N or C–S + S–N transition entropies are plotted against the alkyl chain length in Figure 4. The N–I transition entropies show an odd-even effect, the odd chain lengths being associated with higher values. The C–N or C–S + S–N transition entropies for the homologous series

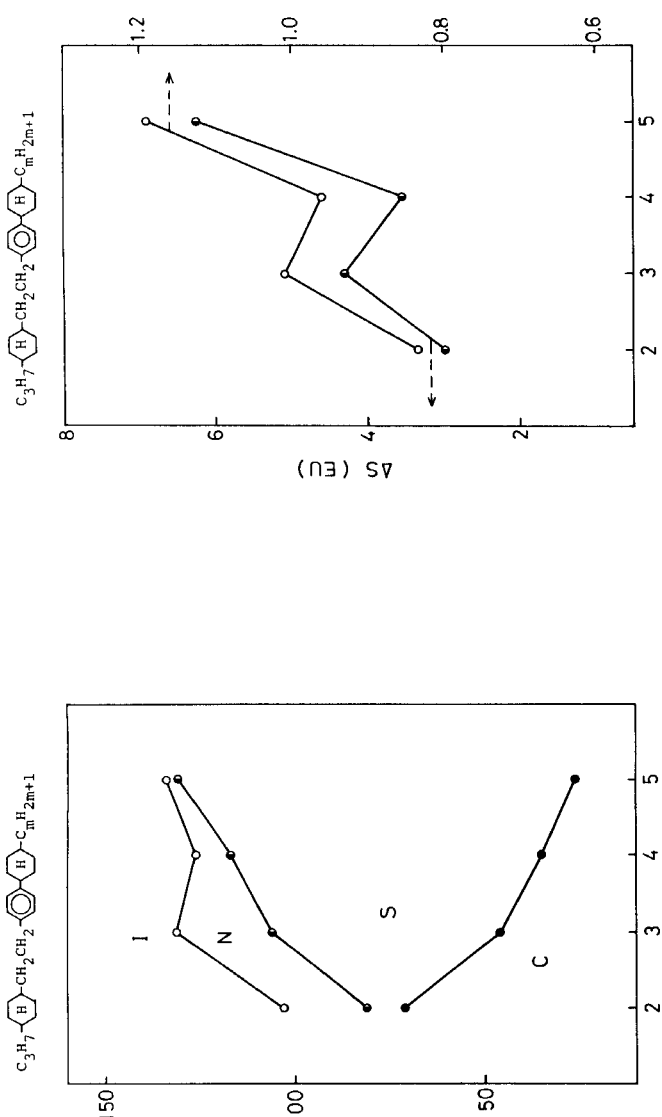


FIGURE 1 Plot of phase transitions against alkyl chain length (m) for the 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes: ●, C–S, ○; S–N, ○; N–I.

FIGURE 2 Transition entropy *vs.* alkyl chain length (m) for the 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-alkylcyclohexyl)phenyl}ethanes: ○; S–N, ○; N–I.

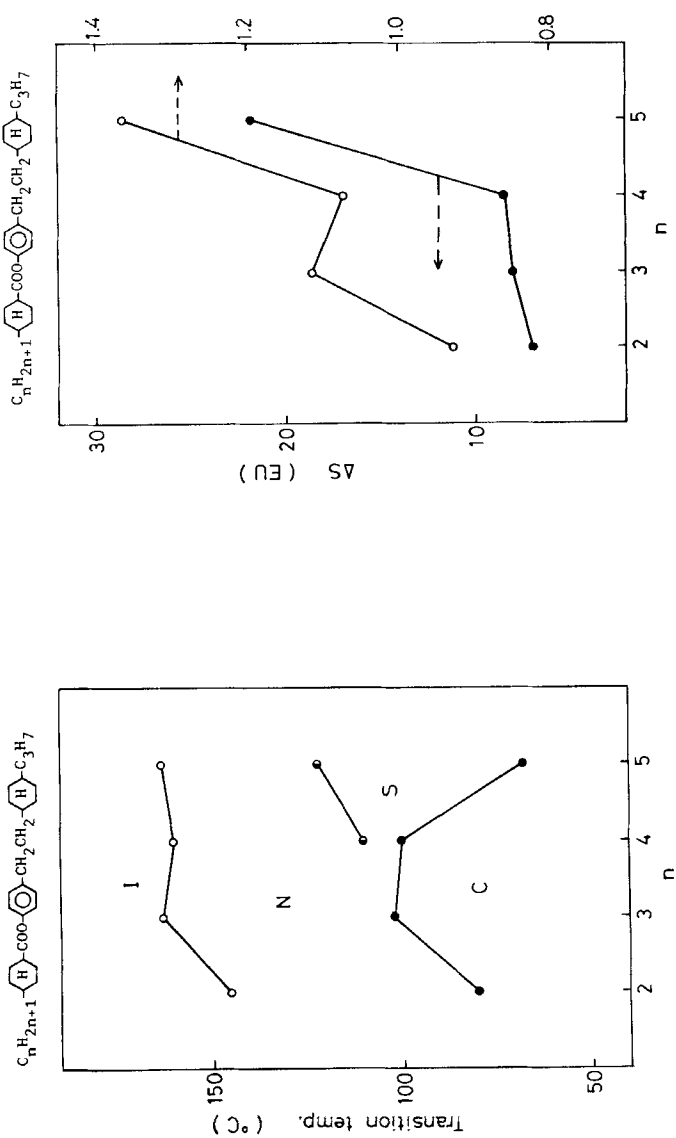


FIGURE 3 Plot of phase transitions against alkyl chain length (n) for the 4-{*β*-(*trans*-4′-*n*-propylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates: ●; C–S or C–N, ○; S–N, ○; N–I.

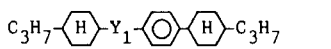
FIGURE 4 Transition entropy *vs.* alkyl chain length (n) for the 4-{*β*-(*trans*-4′-*n*-propylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-alkylcyclohexane-1″-carboxylates: ●; C–N or C–S + S–N, ○; N–I.

from alkyl chain lengths of two to four are almost constant and the entropy for an alkyl chain length of five becomes larger. Similar behaviours are reported for the 4,4′-dialkoxyazobenzenes by Porter *et al.*[5] and for 1-(*trans*-4′-alkylcyclohexyl)-2-(4″-halobiphenyl-4′-yl)ethanes.[6]

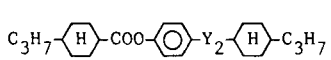
As these compounds do not exhibit nematic phases at room temperature, their flow-aligned viscosities at 20°C and birefringences at 25°C were determined by extrapolation from data obtained using a series of solutions of the compounds in a mixture (A) of 4-*n*-alkoxyphenyl *trans*-4′-*n*-alkylcyclohexane-1′-carboxylates[1] and *trans*-4-*n*-alkyl-1-(4′-cyanophenyl)cyclohexanes.[7] The composition and physical properties of the mixture (A) used as host are given in a previous paper.[6] The viscosity measurements were made using a rotating cone-plate viscometer at 20°C. Birefringences were measured by polarizing microscopy using a compensator.

The N–I transition temperatures, flow-aligned viscosities at 20°C and birefringences at 25°C of the following nematic compounds, which have the same terminal groups and same rings, are compared in order to discuss the influence of the linkage between a phenylene and a cyclohexyl ring in these three ring systems:

System 1 :



System 2 :



The N–I transition temperatures, flow-aligned viscosities at 20°C and birefringences at 25°C of the nematic compounds of system 1 and system 2 are shown in Figure 5 and Figure 6, respectively. Figure 5 shows that the flow-aligned viscosity of 1-(*trans*-4′-*n*-propylcyclohexyl)-2-{4″-(*trans*-4‴-*n*-propylcyclohexyl)phenyl}ethane having the ethylene group (CH_2CH_2) as linkage Y_1 is extremely low compared with that of other nematic compounds having different linkages in system 1. The methyleneoxy linkage (CH_2O) increases the flow-aligned viscosity and raises the N–I transition temperature a little. The carbonyloxy linkage (COO) raises the N–I transition temperature remarkably in the cyclohexane carboxylates. When the oxycarbonyl linkage (OCO) is used as in benzoates, the compound becomes very viscous. Figure 6 shows that the flow-aligned viscosity of 4-{β-(*trans*-4′-*n*-propylcyclohexyl)ethyl}phenyl *trans*-4″-*n*-propylcyclohexane-1″-carboxylate, which has the ethylene group (CH_2CH_2) as linkage Y_2, is the lowest for the nematic compounds of system 2. It is interesting

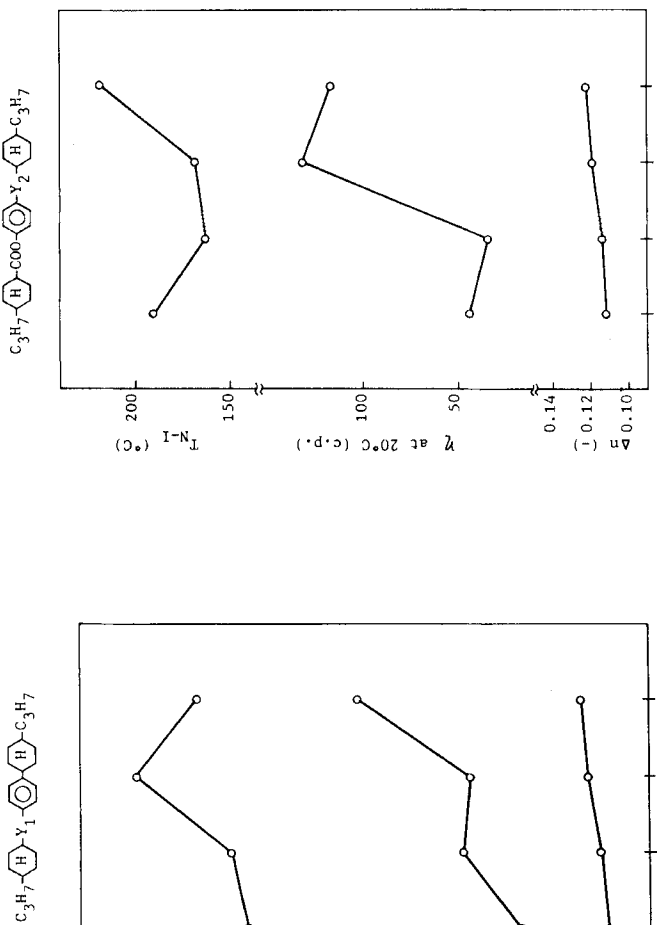


FIGURE 5 N–I transition temperatures (T_{N-I}), flow-aligned viscosities (η) at 20°C and birefringences (Δn) of the nematic compounds having different linkages Y_1 in system 1.

FIGURE 6 N–I transition temperatures (T_{N-I}), flow-aligned viscosities (η) at 20°C and birefringences (Δn) of the nematic compounds having different linkages Y_2 in system 2.

that the flow-aligned viscosity of 4-{β-(*trans*-4′-*n*-propylcyclohexyl) ethyl}phenyl *trans*-4″-*n*-propylcyclohexane-1″-carboxylate is lower than that of 4-(*trans*-4′-*n*-propylcyclohexyl)phenyl *trans*-4″-*n*-propylcyclohexane-1″-carboxylate having no group (−) as the linkage Y_2. The ethylene group therefore reduces the viscosity as a linkage between a phenylene and a cyclohexyl ring. Replacement of the ethylene linkage (CH_2CH_2) by the methyleneoxy linkage (CH_2O) increases the viscosity. The increase for system 2 is larger than that for system 1. The birefringences of the nematic compounds having different linkages for system 1 and system 2 remain almost constant.

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