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Synthesis and Properties of Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer

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SYNTHESIS AND PROPERTIES OF THERMOTROPIC COMPOUNDS WITH TWO TERMINAL MESOGENIC UNITS AND A CENTRAL SPACER

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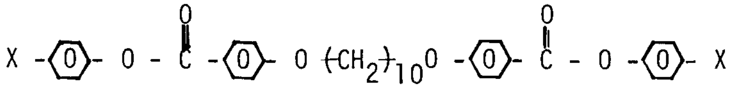
ABSTRACT

A series of liquid crystal compounds which have two identical terminal mesogenic units based on aromatic esters bracketing a central decamethylene spacer in, was prepared, and the thermal properties were examined. The terminal mesogenic uints were principally unsubstituted and substituted p-(phenoxycarbonyl)phenyl ethers.

INTRODUCTION

Thermotropic liquid crystal polymers having alternating rigid mesogenic units and flexible spacers along the main chain are of considerable interest for their structure-property relationships[1,2]. We have previously reported on the synthesis and properties of several such series containing either polymethylene or poly(ethylene oxide) flexible spacers[3-7]. It was also of interest in that study to compare the structure-property relationship of low molecular weight model compounds containing two terminal mesogenic groups attached on either side of a central flexible spacer as shown below:



$$X-\langle O\rangle-O-\overset{O}{\overset{\|}{C}}-\langle O\rangle-O(CH_2)_{10}O-\langle O\rangle-\overset{O}{\overset{\|}{C}}-O-\langle O\rangle-X$$ (1)

X = H, CH_3, Cl, NO_2, CHO, CN, ⟨O⟩

A compound having 2-naphthol moiety in place of p-substituted phenol units, was also included in this study. Recently Griffin and Britt in a similar investigation, reported the formation of enantiotropic nematic phases from symmetric diesters of 4.4'-dihydroxy-1,10-diphenoxydecane[8].

RESULTS AND DISCUSSION

The influence of terminal substituents on liquid crystal behavior has been systematically evaluated for a great many series of compounds, but very few studies describing the structure-property relationship for the type of compounds above have been reported[9].

All of the compounds, except the 2-naphthol derivative, in the present investigation showed two endothermic peaks in the thermograms obtained by differential scanning calorimetry, DSC, as shown in Table 1. Examination on the hot stage of a polarizing microscope revealed that the first peak corresponded to a melting, T_{K-N}, and the second to a liquid crystal - to - isotropic phase transition, T_{N-I} (clearing temperature). Only nematic optical textures could be observed for these compounds, and all transitions were reversible.

In contrast to the results in Table 1 for the substituted phenyl esters, the 2-naphthyl ester derivative showed only one endothermic peak at 166°C on heating in the DSC thermogram, but two exotherms were formed on

TABLE 1. Transition temperatures of 1, 10- bis (4-p-substituted phenoxycarbonyl)phenoxydecane (1)

Substituent	T_{K-N},°C	T_{N-I},°C	ΔT,°C
H	121.5	127.5	6
CH_3	137	146	9
Cl	146	156	10
NO_2	144	160	16
CHO	150.5	162.5	12
CN	158	181	23
C_6H_5	183	212	29
2-Np[a]	166		
	127[b]	148[b]	21[b]

[a] 2-Naphthol ester.

[b] Values obtained from the cooling curve on DSC.

cooling, the first at 148°, and the second 127°C. Examination with the polarizing microscope revealed that this compound was transformed from a crystalline solid directly into an isotropic liquid on heating, but on cooling the isotropic liquid formed a nematic liquid crystal phase before crystallization; that is, this compound appeared to be monotropic.

In general as seen in Table 1, the melting and clearing temperatures increased in a uniform manner for the series of substituents, and the ability of substituents to stabilize the mesophase followed the following order:

$$H < CH_3 < Cl < CHO < NO_2 < CN < C_6H_5.$$

This order is in good agreement with the data for other types of thermotropic liquid crystal compounds[9]. Gray explained substituent effects on nematic phase stability on the basis of either enhanced polarizability or increased polarity of the mesogenic units by the presence of the substituents[10], and the results for the present series is consistent with such an explanation, excepting the effect of the phenyl and naphthyl groups. For these two groups the increased length of the mesogenic unit is probably the most important factor.

It is rather interesting that the 2-naphthol ester was monotropic while the phenyl ester was enantiotropic. A thermodynamic study of the phase transitions of these compounds is now in progress, but preliminary results indicate that the 2-naphthol derivative had a considerably higher heat of melting than that of the phenyl derivative which resulted in the direct transition from the crystal to the isotropic phase[11].

EXPERIMENTAL

Preparation of Compounds

1,10-Bis(4-carboxyphenoxy)decane[2] (5g; 0.12 mole) was refluxed with 17 ml. of thionyl chloride for 4 hours. Excess thionyl chloride was removed at room temperature by vacuum distillation. The solid diacid dichloride was dissolved in 30 ml. dry pyridine, and 0.024 moles of either the p-substituted phenol or 2-naphthol was added. The mixture was stirred at room temperature for 9 hours and then at 70°C for an additional one hour. The reaction mixture was poured with rapid agitation into cold water. The precipitate was thoroughly washed with water and dried, and the crude product was recrystallized from a toulene-95% ethanol solution and dried at 90°C. Yields ranged from 85 to 95%.

Characterization of Compounds

The structures of the compounds were verified by elemental analysis and IR and NMR spectroscopy. The thermal behavior of each compound was evaluated on a Perkin-Elmer DSC-1B and on a hot-stage (Mettler FP-2) of a polarizing microscope. Heating and cooling rates were maintained at 20°C/min for DSC analysis. All of the DSC thermograms were obtained under a nitrogen atmosphere.

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