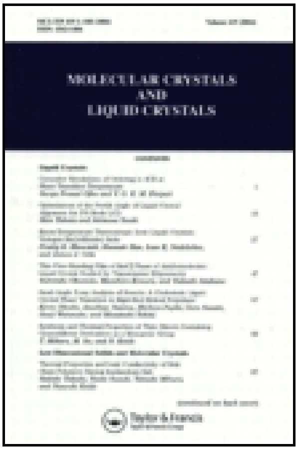

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# Synthesis and Thermotropic Properties of Dimesogenic Homologous Series Containing Disiloxyl Spacer, DI-4- (P-Substituted Phenoxycarbonyl) Phenoxymethyl Tetramethyl Disiloxanes

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# SYNTHESIS AND THERMOTROPIC PROPERTIES OF DIMESOGENIC HOMOLOGOUS SERIES CONTAINING DISILOXYL SPACER, DI-4-(P-SUBSTITUTED PHENOXYCARBONYL) PHENOXYMETHYL TETRAMETHYL DISILOXANES*

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Summary A new series of thermotropic compounds having two terminal, aromatic dyad ester-type mesogenic units and a disiloxyl spacer were prepared and their liquid crystalline properties were studied. The mesogenic units of these compounds were p-substituted phenyl-p-oxybenzoates with different substituents such as H, $CH_3$, $OCH_3$, $C_6H_5$, Cl, CN and $NO_2$. $\beta$-Naphthyl-p-oxybenzoyl containing compound also was included in this series. All of the compounds were found to be smectic. The nature of the smectic mesophase depends on the structure of the p-substituent. The mesophase temperature range was fairly narrow between 10 to 30°C. The compounds' heats of melting were very low compared with other dimesogenic compound, e.g. those having polymethylene spacers.

## INTRODUCTION

Thermotropic compounds having two terminal mesogenic units and a central flexible spacer are not only interesting as a new class of liquid crystalline compositions per se[1,2] but also are known to be excellent model compounds for the thermotropic main chain polymers consisting of the similar mesogenic unit and spacers.[3,4] Many series of dimesogenic compounds with variety of structures were reported earlier by us

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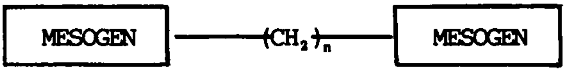
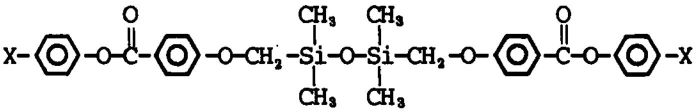
*For the previous of this series refer to J.-I. Jin, E-J. Choi and B.-W. Jo, Polymer (Korea), 10(6), 635 (1986).

and by others.[1-4] We also recently reported the mutual miscibility in mesophase of these compounds[5] and of these compounds and main chain thermotropic polyesters.[6] All of the compounds reported by us, however, contain polymethylene spacers.



In this report we would like to describe the preparation and properties of dimesogenic compounds having a disiloxyl spacer with the following structure :



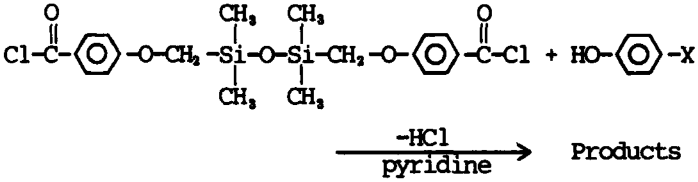
X = H, $CH_3$, $OCH_3$, Cl, CN, $NO_2$ and $C_6H_5$

The compound in which p-substituted phenyl unit is replaced by β-Naphthyl group also is included in the present series. Main chain thermotropic poly-and copolyesters having di-and oligosiloxyl spacers have been reported by us[7-9] and others.[10] They tend to have low transition temperatures and a low degree of crystallinity, compared with those having polymethylene spacers. Therefore, we also were interested in comparing the properties of the present compounds with polyesters containing disiloxyl spacers.

## EXPERIMENTAL

### SYNTHESIS OF THE COMPOUNDS

The final compounds, di-4-(p-substituted phenoxycarbornyl) phenoxymethyltetramethyldisiloxanes, were prepared by reacting bis-(p-chloroformyl-phenoxymethyl)tetramethyldisiloxane[7] with p-substituted phenols in pyridine, which acted as a solvent and an HCl-acceptor.



The bischloroformyl compounds were prepared following our earlier procedure[7], from dibromomethyltetramethyldisiloxane and ethyl 4-hydroxybenzoate, followed by hydrolysis and reaction with $SOCl_2$. Since the procedure used for the last step of the synthetic scheme was all same for all propducts, only a representative method is given : The dichloroformylcompound (0.01mole) was dissolved in 30ml of dry pyridine. To this solution was added 0.02moles of a p-substituted phenol at room temperature. The mixture was stirred under a $N_2$ atmosphere for 3 hours at room temperature and then for another 2 hours at 70°C. The reaction mixture was poured into large excess of distilled water and the white precipitate was collected in a filter. The compounds with X=H and $NO_2$ were recrystallized from pyridine and all the others from ethanol.

## STRUCTURE IDENTIFICATION AND CHARACTERIZATION OF LIQUID CRYSTALLINE PROPERTIES

The structures of the compounds were confirmed by elemental analysis performed by the Microanalytical Laboratory of the University of Massachusetts and the Analytical Laboratory of Sam-Hwa Chemicals, Ind., Korea. IR spectra of KBr pellets were obtained on a Shimadzu IR-440 and $H^1$-and $C^{13}$-NMR spectra in $CDCl_3$ on a Bruker SY-80. For $H^1$-NMR spectra, the spectrometer frequency was 80MHz and for $C^{13}$-NMR spectra, it was 20.15MHz. Thermal and liquid crystalline properties of the compounds were examined on a differential scanning calorimeter (Mettler TA 3000) at a heating and cooling rate of 10°C/min and on a polarizing microscope (Leitz, Ortholux) equipped with a Mettler FP-52 hot stage. In DSC analysis, indium was employed as a standard for temperature calibration. The peak maxima temperatures on the DSC thermogram obtained from heating runs were taken as melting (Tm) and isotropization temperatures (Ti).

## RESULTS AND DISCUSSION

### SYNTHETIC RESULTS AND CONFIRMATION OF STRUCTURES

The product yields and results of elemental analyses are given in Table 1. The yields are generally high, ranging from 88 to 94% and analytical results are in good agreement with expected values. The experimental percentages of Si are slightly lower than the theoretical values.

Table 1 Yields and Results of Elemental Analyses

| Compound | Yield | Elemental Analysis[a], wt.% | | | | |
|---|---|---|---|---|---|---|
| X | wt.% | C | H | Si | N | Cl |
| H | 97 | 64.9<br>(65.5) | 5.7<br>(5.8) | 9.3<br>(9.6) | | |
| $CH_3$ | 96 | 65.2<br>(66.4) | 6.4<br>(6.2) | 8.8<br>(9.1) | | |
| $OCH_3$ | 90 | 62.6<br>(63.1) | 6.0<br>(5.9) | 8.5<br>(8.7) | | |
| Cl | 92 | 56.7<br>(58.6) | 5.2<br>(4.9) | 8.4<br>(8.6) | | 10.7<br>(10.8) |
| CN | 95 | 63.6<br>(64.1) | 5.1<br>(5.1) | 8.6<br>(8.8) | 4.4<br>(4.4) | |
| $NO_2$ | 95 | 56.1<br>(56.8) | 5.2<br>(4.8) | 8.0<br>(8.3) | 4.0<br>(4.1) | |
| $C_6H_5$ | 87 | 69.9<br>(71.5) | 5.8<br>(5.7) | 7.5<br>(7.6) | | |
| β-Naph | 86 | 69.2<br>(71.5) | 5.7<br>(5.5) | 8.0<br>(8.2) | | |

[a] The values in parentheses are theoretical ones

However, it is well known that analytical result for Si obtained through oxidation to $SiO_2$ is frequently less than satisfactory. All of the IR and NMR spectra were consistent with the expected structures of the compounds. Figures 1-3 show IR, $H^1$-NMR and $C^{13}$-NMR spectra of the compound with X=CN. The IR spectrum (Figure 1) shows a-C≡N stretching absorption at 2210cm$^{-1}$; >C=O absorption at 1723cm$^{-1}$, aromatic C=C mode at 1595cm$^{-1}$, and $-\overset{|}{\underset{|}{Si}}-CH_2-$and $CH_3-\overset{|}{\underset{|}{Si}}-CH_3$ vibrations at 1410 and 1260cm$^{-1}$, respectively. A strong absorption due to $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-$ vibration is observed at 1058cm$^{-1}$. Other absorption bands such as -C-O-(1217cm$^{-1}$) and aromatic C-H out-of plane bending (827cm$^{-1}$) are also observed. The $H^1$-NMR spectrum (Figure 2) also is fairly simple; it shows $-\overset{|}{\underset{|}{Si}}-CH_3$ proton resonance at $\delta$0.27 (singlet), $-O-CH_2-\underset{|}{Si}-$ resonance at $\delta$2.36 (singlet) and aromatic protons resonance at $\delta$6.92-7.25 (multiplet). These all are in accord with the anticipated structure. The proton decoupled $C^{13}$-NMR spectrum (Figure 3) shows 12 well separated peaks consistent with the expected structure. Only the resonance peaks corresponding to $C_4$ and $C_{11}$, and also of $C_6$ and $C_8$ are located very close to each other. However, even these are distinct and individually identifiable. The exact resonance positions are recorded in the spectrum.

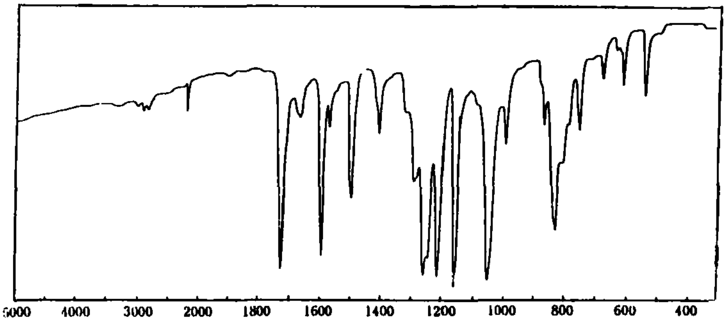


Figure 1. IR spectrum of the compound with X=CN

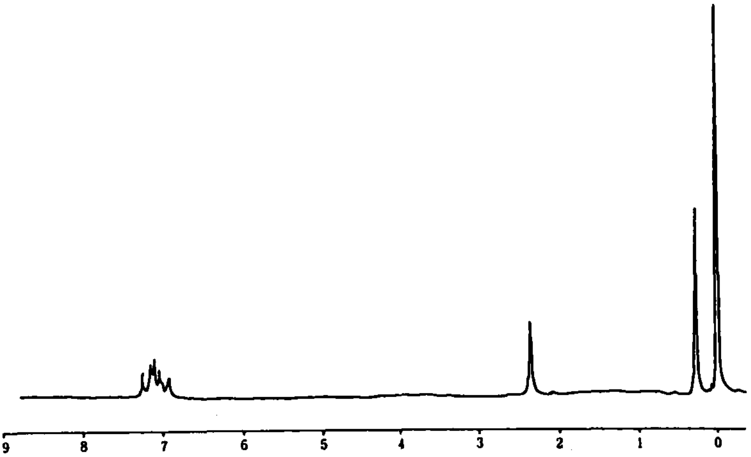
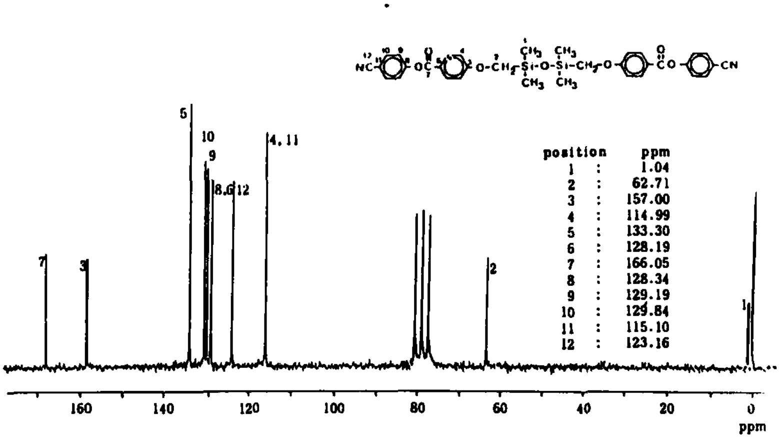


Figure 2. $H^1$-NMR spectrum of the compound with X=CN (in $CDCl_3$).



| position | | ppm |
|---|---|---|
| 1 | : | 1.04 |
| 2 | : | 62.71 |
| 3 | : | 157.00 |
| 4 | : | 114.99 |
| 5 | : | 133.30 |
| 6 | : | 128.19 |
| 7 | : | 166.05 |
| 8 | : | 128.34 |
| 9 | : | 129.19 |
| 10 | : | 129.84 |
| 11 | : | 115.10 |
| 12 | : | 123.16 |

Figure 3. Proton-decoupled $C^{13}$-NMR spectrum of the compound with X=CN(in $CDCl_3$).

## THERMAL TRANSITIONS AND LIQUID CRYSTALLINE PROPERTIES

All of the compounds, with the exception of those with X=$OCH_3$ and $NO_2$, exhibited two well separated endotherms (Figure4) on the DSC heating cycle runs. The lower temperature endotherms correspond to solid-to-mesophase transitions and the higher temperature ones to mesophase-to-isotropic liquid transitions.

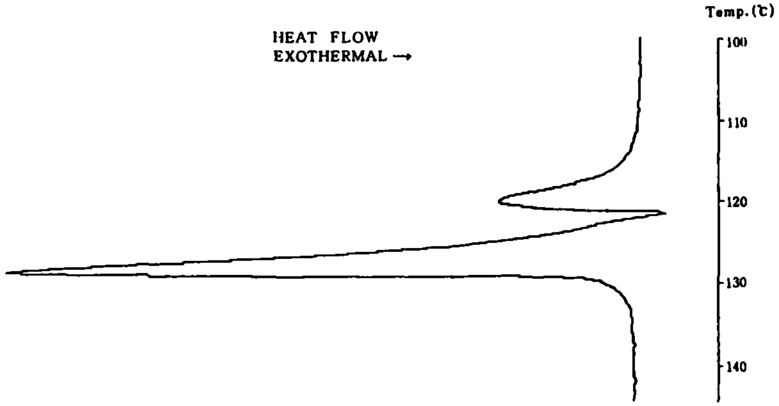


Figure 4. DSC thermogram of the compound with X=CN. The heating and cooling rate were 10°C/min.

These phase transitions also were confirmed by microscopic observations. All of the compounds are enantiotropic and form only one mesophase in the melt. Table 2 shows the melting (Tm) and isotropization temperatures (Ti) of the compounds together with thermodynamic parameters values for the transitions. This table also shows the mesophases that each compound forms. According to the Ti data given in Table 2, the smectic group efficiency, of the substituents, in other words, the ability of substituents to stabilize the mesophase, is in the order of $H < CH_3 < Cl \approx NO_2 < CN < OCH_3 < C_6H_5$. This order is generally in good agreement with those found in many series of monomesogenic compounds[11] and with that found in a series of dimesogenic compounds reported earlier by us[1].

Table 2 Thermal and Liquid Crystalline Properties

| Compound<br>X | Tm<br>°C | Ti<br>°C | $\Delta$Hm<br>J/g | $\Delta$Hi<br>J/g | $\Delta$Hi/$\Delta$Hm<br>% | L.C.Prop.<br>mesophase |
|---|---|---|---|---|---|---|
| H | 52 | 75 | 18.7 | 18.5 | 99 | $S_B$ |
| $CH_3$ | 97 | 114 | 41.8 | 18.0 | 43 | $S_B$ |
| $OCH_3$ | 118 | 128 | (24.3)[a] | (12.5)[a] | 136 | $S_B$ |
| Cl | 95 | 118 | 39.1 | 14.1 | 36 | $S_B$ |
| CN | 106 | 124 | 16.4 | 62.4 | 380 | $S_B$ |
| $NO_2$ | 90 | 118 | (27.5)[a] | (17.8)[a] | 219 | $S_A$ |
| $C_6H_5$ | 142 | 158 | 45.6 | 32.3 | 71 | $S_B$ |
| β-Naph | 113 | 125 | 18.8 | 20.9 | 111 | $S_B$ |

[a] values obtained from cooling DSC curves, because the two peaks overlapped each other on the heating curves. The cooling rate was 10°C/min.

β-Naphthyl structure appeared to be as efficient as p-anisyl group (i.e. X=$OCH_3$) in stabilizing the mesophase. A striking difference between the present compounds and main chain thermotropic polyesters consisting of aromatic dyad or triad ester-type mesogenic units and disiloxyl or oligosiloxyl spacers[7-10] lies in the fact that the former form smectic phases while the latter form nematic phases. It seems to be a general phenomenon that smectic mesophase formation is easier for low molar mass compounds than for polymers having similar structures as repeating units. This may be due to the much higher degree of freedom of low molar mass molecules in the melt enabling them to organize an ordered structure of high regularity. Such a freedom is much less likely to exist in polymers whose chains are tend to entangle and whose mesogenic units are tied up to each other through spacers. Their mobility to form highly ordered structure, therfore, is under much severer contraints. Another interesting point to be emphasized is the fact that the heats of melting, $\Delta$Hm's, of the disiloxyl compounds are extremely low compared with those of dimesogenic compounds with polymethylene spacers. The values of $\Delta$Hm's for the present series range from about 16 to 45 J/g, while those with polymethylene spacers are in the order of 100 J/g.[1,2] The values of $\Delta$Hi, the heats of isotropization, however, are comparable. Thus, the ratios of $\Delta$Hi to $\Delta$Hm for the disiloxyl compounds are very high ranging from 0.3 to 3 (Table 2). It has been reported that this ratio for other dimesogenic compounds with polymethylene spacers are in the range of 0.1.[1,2] This indicated that the present compounds form crystalline solids whose lattice force and molecular attractions are very low. This probably is due to the large substituent size and the extremely low rotational energy barrier of the disiloxyl spacer.

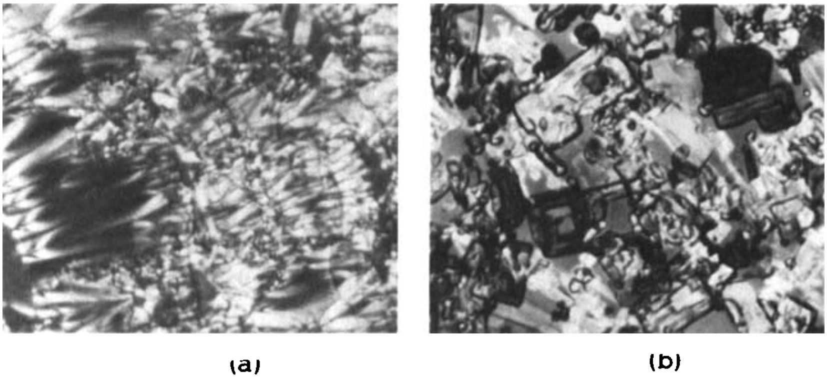

(a) (b)

Figure 5. Optical textures of (a) the compound with X=$NO_2$ taken at 98°C and (b) of the compound with X=CN taken at 118°C (both, magnification X 320).

We observed that all of the compounds remained in mesophases even at room temperature for more than one hour when their isotropic melts were cooled down. Figure 5 shows the $S_A$ texture observed for the compounds with X=$NO_2$ (a) and the $S_B$ texture observed for X=CN (b) as well as all the other compounds in the series. The optical texture shown in Figure 5a is the so-called "focal conic" type; the one shown in Figure 5b is a mosaic texture.[12]

## CONCLUSION

1. A series of new dimesogenic compounds, di-4-(p-substituted phenoxycarbonyl)phenoxymethyl tetramethyldisiloxanes, were prepared and were identified.
2. All of the compounds are enantiotropic and form smectic phases in melts. The compounds with X=$NO_2$ is $S_A$ while the remaining ones are $S_B$.
3. The heat of melting, $\Delta$Hm, is particularly low, while the heat of isotropization, $\Delta$Hi, was comparable to other dimesogenic compounds.

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