

Synthesis and Liquid Crystalline Properties of the Compounds Consisting of a Schiff Base Type Mesogen and a Dyad Type Aromatic Ester Structure Interconnected Through the Central Hexamethylene Spacer

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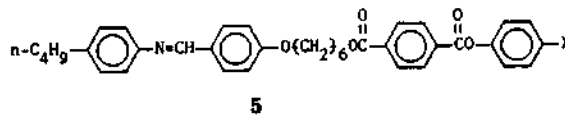
A series of compounds consisting of 4'-oxybenzylidene-4-*n*-butylaniline, a mesogen, and a *p*-substituted phenoxyterephthaloyl structure a non-mesogen, interconnected through a central hexamethylene spacer were synthesized and their thermal behavior and liquid crystallinity were studied. *p*-Substituents included in this study are H, Cl, CN, NO₂, *n*-C₄H₉O and phenyl groups. The compounds having phenyl and *n*-C₄H₉O substituents are enantiotropic and form smectic-A(S_A) and nematic (N) phases. The compound with NO₂ substituent is monotropic and forms only a nematic phase on heating the solid, whereas it forms nematic as well as S_A phases on cooling the isotropic liquid. The rest compounds were found to be non-liquid crystalline. This is in great contrast to the fact that the monomesogenic model compound 4'-*n*-hexyloxybenzylidene-4-*n*-butylaniline forms S_B, S_C, S_A and N phases enantiotropically.

Introduction

Dimesogenic compounds that have two identical terminal mesogenic units linked through a central spacer reveal very interesting properties¹⁻⁸: 1) they exhibit a clear odd-even effect in melting (T_m) and isotropization (T_i) temperatures when the spacer is polymethylene unit, 2) their liquid crystalline temperature ranges appear to be narrower than those of the corresponding monomesogenic counterparts mainly due to the fact that enhancement in T_m by the presence of two rigid mesogens surpasses the extent of increase in T_i , 3) the group efficiency in stabilizing mesophases by the terminal substituents are very similar to that observed in monomesogenic compounds, 4) the heat of isotropization (ΔH) is significantly higher than that of monomesogenic counterpart, which is particularly so when the central spacer is disiloxyl unit⁶, and 5) they, like the monomesogenic compounds, follow the selective miscibility rule proposed earlier by Sackmann and Demus.⁹

In addition, thermal transition behavior of dimesogenic compounds of a homologous series was found to simulate very well the thermal properties of the corresponding series of main chain liquid crystalline polymers having the same flexible spacers and the similar mesogenic units.³ In contrast, it, however, was reported earlier by us¹⁰ that the dimesogenic compounds with a fixed length of the central spacer, but having alkyl terminal substituents of varying length are quite different in thermal transition behavior and in the nature of mesophases they form.

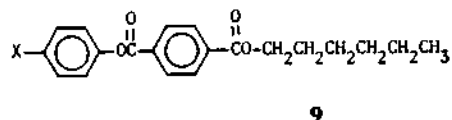
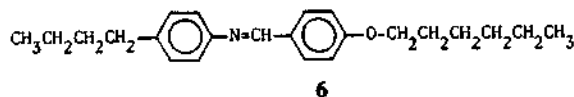
As a part of our continuing efforts to delineate the structure-property relationship of thermotropic compounds, we synthesized a series of compounds that have two different, terminal rigid units interconnected through the central hexamethylene spacer. It is our understanding that this is the first report describing the liquid crystalline properties of the compounds of this type. The structure of the compounds is presented below: The mesogenic units on the left-hand side correspond to N-(4-*n*-alkyloxybenzylidene)-4-*n*-butylanilines, that form nematic as well as smectic phases.^{11,12} The



X = C₆H₅, *n*-C₄H₉O, NO₂, CN, Cl, and H.

other terminal, rigid units on the right-hand side of the compounds are of aromatic ester type structures, which are non-mesogenic as will be described later. We wanted particularly to investigate whether the two terminal units would contribute separately or cooperately in the formation of mesophases.

For comparison purpose, we synthesized the following monomeric compounds and their mesomorphic properties also were examined. Synthesis and thermal behavior of the



X = C₆H₅, *n*-C₄H₉O, NO₂, CN, Cl and H

compound 6 were reported by others,^{11,12} but we found some discrepancy in the literature data. Therefore, we again prepared this compound to reinvestigate its thermal and liquid crystalline properties.

Experimental

Synthesis.

Since the synthetic methods of the compounds 5 are more or less the same, one representative detail is described below for the preparation of N-[4-{6-(*p*-butoxyphenoxy)carbonyl}benzoyloxy]hexyloxybenzylidene-4-*n*-butylaniline, in

other words, the compound 5 with $X = n\text{-C}_4\text{H}_9\text{O}$.

N-(4-Hydroxybenzylidene)-4-*n*-butylaniline(1).

Ethanol solution (140 ml) of 4-hydroxybenzaldehyde (15.3g; 0.125 mole) and 4-*n*-butylaniline (18.8g; 0.126 mole) was refluxed for 2 hours. The solution was chilled in an ice-water bath and the precipitate formed was collected on a filter. The crude product was recrystallized from ethanol. The yield was 28.5g (90.0%) m.p., 173–174 °C.

N-(4-(6-Hydroxyhexyloxy)benzylidene)-4-*n*-butylaniline(2). The above prepared compound 1 (18.0g; 0.0710 mole) together with 9.70g (0.0710 mole) of 6-chloro-1-hexanol was dissolved in 35 ml of *N,N*-dimethylformamide(DMF) containing 3.76g (0.0355 mole) of Na_2CO_3 . The mixture was heated to and maintained at 135 °C overnight. The solution was poured into distilled water and the precipitate was collected on a filter followed by washing with 1M NaOH and distilled water. The crude product was recrystallized from *n*-hexane. Yield was 12.8g (51.0%); m.p., 62 °C.

4-(*p*-Butoxyphenoxycarbonyl)benzaldehyde(3). 4-Carboxybenzaldehyde (5.10g; 0.0340 mole) first was converted to acid chloride by refluxing in SOCl_2 followed by removing the excess SOCl_2 . The acid chloride formed was dissolved in a mixture of DMF (5 ml) and pyridine (5 ml). To this solution was added 4-butoxyphenol (5.65g; 0.0340 mole) dissolved in 10 ml of DMF. The mixture, after being kept at room temperature overnight, was poured into 0.1M NaOH. The precipitate was washed with distilled water. The crude product was recrystallized from chloroform. Yield was 9.23g (91.0%); m.p., 85 °C.

4-(*p*-Butoxyphenoxycarbonyl)benzoic acid(4). 4-(*p*-Butoxyphenoxycarbonyl) benzaldehyde (8.95g; 0.0300 mole) and 1g of dibenzo-18-crown-6(DBC) were dissolved in 50 ml of 1,2-dichloroethane. This solution was mixed with 20 ml solution of KMnO_4 (6.64g; 0.0420 mole) and the mixture was stirred vigorously at 60 °C for 4 hours. The precipitate was collected on a filter and washed with DMF. And the filtrate was concentrated using a rotatory evaporator and the solution was acidified with 1M HCl. The precipitate was washed with water and recrystallized from ethanol. Yield was 5.84g (62.0%); m.p., 198 °C.

N-[4-{6-(*p*-Butoxyphenoxycarbonyl)benzoyloxy}hexyloxybenzylidene]-4-*n*-butylaniline (5; $X = n\text{-C}_4\text{H}_9\text{O}$). 4-(*p*-Butoxyphenoxycarbonyl)benzoic acid chloride prepared from 4(6.45g; 0.0205 mole) and SOCl_2 was dissolved in 50 ml of pyridine. N-{4-(6-Hydroxyhexyloxy)benzylidene}-4-*n*-butylaniline(2) (7.25g; 0.0205 mole) was dissolved in this solution. The solution was stirred at room temperature overnight, and then poured into ethanol. The precipitate was washed with chloroform and extracted with toluene at room temperature. Toluene was evaporated and the residue was recrystallized from *n*-butanol. $^1\text{H-NMR}$ spectrum ($\text{DMSO-d}_6/\text{TMS}$); δ 0.8–2.0 (m, 15H, $-\text{CH}_2-$, and $-\text{CH}_3$), δ 2.4–2.6 (t, 2H, $-\text{CH}_2-\text{C}_6\text{H}_4-$), δ 3.8–4.4 (sex, 4H, $-\text{OCH}_2-$), δ 7.0–8.2 (m, 21H, Ar), δ 8.6 (s, 1H, $-\text{N}=\text{CH}-$). IR spectrum (KBr); aromatic C-H stretching at 3050–3150 cm^{-1} , C-H stretching at 2850–3000 cm^{-1} , $-\text{C}=\text{O}$ stretching at 1715 and 1710 cm^{-1} , $-\text{C}=\text{N}$ -stretching at 1650 cm^{-1} , aromatic $-\text{C}=\text{C}$ - stretching at 1615 cm^{-1} and C-O stretching at 1280, 1100 and 1020 cm^{-1} . Yield was 8.13g (61.0%); m.p., 128 °C. The yields of other compounds were 43% for $X = \text{Ph}$,

Table 1. Yields and Melting Points of Compounds 9

X	Yield, %	M.P., °C
H	86.6	43
Cl	87.6	49–50
CN	84.3	57–58
<i>n</i> -C ₄ H ₉ O	83.2	47–48
C ₆ H ₅	81.9	117

65% for $X = \text{NO}_2$, 56% for $X = \text{CN}$, 49% for $X = \text{Cl}$ and 72% for $X = \text{H}$, respectively. Recrystallization solvents are included in Table 2.

N-(4-Hexyloxybenzylidene)-4-*n*-butylaniline(6).

The compound 1(3.03g; 12.0 mmole) and 0.63g (6.0 mmole) of sodium carbonate were dissolved in 20 ml of DMF. To this solution added was 1.98g (12.0 mmole) of 1-bromohexane. The mixture was stirred vigorously at 135 °C for 24 hours. The reaction mixture was then poured into a large excess aqueous 0.5M Na_2CO_3 solution. The precipitate was washed thoroughly with water. The crude product was recrystallized from ethanol. Yield was 1.85g (46.0%). m.p. 34–35 °C.

Mono-*n*-hexylterephthalate(8). Di-*n*-hexylterephthalate 7(58.5g; 0.175 mole) prepared from terephthaloyl chloride and 1-hexanol was dissolved in 200 ml of 1-hexanol and the mixture was heated to 80 °C. To this solution added dropwise with vigorous stirring was potassium hydroxide (11.8g; 0.210 mole) solution dissolved in 60 ml of 1-hexanol. The mixture was stirred at 80 °C for one additional hour. After the mixture was cooled to room temperature the precipitate was collected on a filter and washed with acetone. The precipitate was dissolved in distilled water and the solution was acidified with 1M HCl. The precipitate was extracted with acetone and only the acetone soluble fraction was collected. After acetone was removed by evaporation using a rotatory evaporator, the solid residue was washed thoroughly with water. The crude product was recrystallized from ethanol. Yield was 21.0g (48.0%); m.p., 105–106 °C.

4-Nitrophenyl-*n*-hexylterephthalate(9; $X = \text{NO}_2$).

The compound 8(2.60g; 1.04 mmole) was dissolved in 10 ml of SOCl_2 and the solution was refluxed for 4 hours. The excess SOCl_2 was removed by distillation under a reduced pressure. Mono-*n*-hexylterephthaloyl chloride thus prepared and 1.45g (1.04 mmole) of *p*-nitrophenol were dissolved in 16 ml of 1,2-dichloroethane containing 1 ml of pyridine that was prechilled an ice-water bath. After the ice-water bath was removed, the reaction mixture was stirred overnight at room temperature under a N_2 atmosphere. Dichloroethane was removed by distillation and the residue was dissolved in acetone. The acetone solution was added dropwise to 0.1M HCl precipitating the product, which then was recrystallized from ethanol. Yield was 3.43g (88.7%) m.p., 53–54 °C. The rest of the series of compounds 9 were synthesized *via* the same synthetic method and their yields and m.p.'s are as shown in Table 1.

Structural Analysis

Structures of the intermediates and the final compounds were confirmed by elemental analysis (Table 2) and by IR (Perkin Elmer 710B) and NMR (Varian EM 306A) spectroscopy. Elemental analysis was conducted by the Analytical Department of the Korea Research Institute of Chemical

Table 2. The Results of Elemental Analyses

Compounds	Elemental Contents, wt. %			Recrystallization solvent
	C	H	N	
5(X = C ₆ H ₅)	79.15(79.01)	6.49(6.58)	2.10(2.14)	toluene/DMSO
5(X = <i>n</i> -C ₄ H ₉ O)	72.03(71.38)	6.11(6.10)	4.48(4.50)	<i>n</i> -butanol
5(X = NO ₂)	75.76(75.80)	7.24(7.24)	2.12(2.15)	toluene
5(X = CN)	79.76(79.74)	6.35(6.31)	4.54(4.65)	toluene
5(X = Cl)	71.58(72.60)	6.18(6.21)	2.27(2.28)	toluene
5(X = H)	76.89(76.94)	6.76(6.75)	2.42(2.42)	<i>n</i> -butanol
6	81.80(81.83)	9.40(9.28)	4.04(4.15)	ethanol
9(X = C ₆ H ₅)	77.85(77.58)	6.53(6.52)	—	methanol
9(X = <i>n</i> -C ₄ H ₉ O)	71.83(72.32)	7.69(7.60)	—	ethanol
9(X = NO ₂)	64.22(64.67)	5.81(5.71)	3.68(3.77)	ethanol
9(X = CN)	71.57(71.77)	6.21(6.03)	3.97(3.99)	methanol
9(X = Cl)	66.37(66.56)	5.89(5.88)	—	methanol
9(X = H)	73.04(73.59)	6.83(6.81)	—	ethanol

^aThe values in the parentheses are the calculated ones for the molecular formulas.

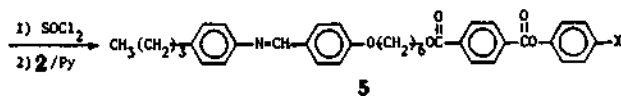
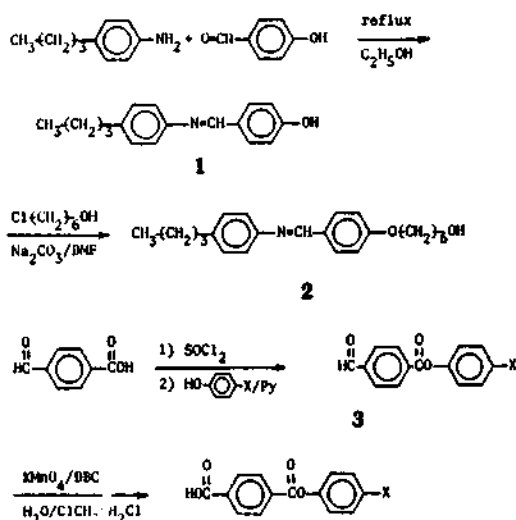
Technology. IR and NMR spectral data were consistent with the expected structures. Since no unusual spectral results were observed, the spectral data were given in this part only for the compound 5 with X = *n*-C₄H₉O.

Thermal Transition and Optical Textures

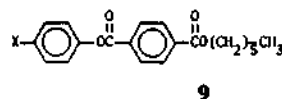
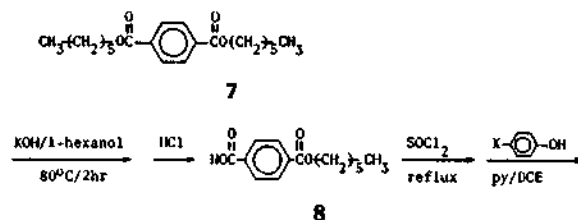
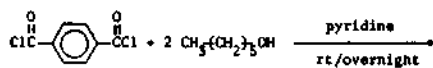
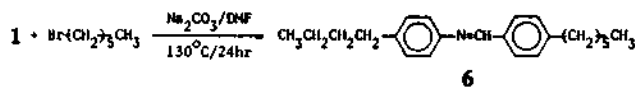
Thermal behavior of the compounds was studied under a N₂ atmosphere on a DuPont's differential scanning calorimeter (DSC) model 910 with a heating or cooling rate of 10°C/min. The optical textures of the melts were examined on a cross-polarizing microscope (Leitz, Ortholux) equipped with a Mettler hot stage FP-2. Magnification was 300X. Indium was employed as a reference for estimation of thermodynamic parameters for the phase transitions.

Results and Discussion

Synthesis of Compounds. The synthetic route of the compound 5 is rather straightforward and each reaction step is of relatively well know type. Their synthetic scheme is give below:



Experimental part describes the synthesis of compound 5 having X = *n*-C₄H₉O. Other homologues having different substituents on the phenyl ring of the aromatic ester type rigid structure were synthesized similarly using the required *p*-substituted phenols in the preparation of 3 homologues. In order to compare the liquid crystalline properties of the present compounds 5 with those of the corresponding monomesogenic compounds the compounds 6 and 9 were prepared via the following routes:



The detailed procedures for the preparation of the compounds 6 and 9 are described in the Experimental part.

The results of elemental analysis (Table 2) are in excellent accord with calculated values for the expected, final compounds. All of the IR spectra of the compounds revealed C=O(1704, 1730 cm⁻¹) and C=N(1650 cm⁻¹) stretching vibrational absorptions. Other spectral features were consistent with those of expected structures for all of the compounds. NMR spectra also were consistent with the structures of the compounds.

Thermal Behavior. The thermal behavior of the compounds was studied by differential scanning calorimetry (DSC). And it was found that their thermal behavior is extremely sensitive to the nature of the substituent X. The two compounds 5 having X = Ph and *n*-C₄H₉O exhibited three endothermic peaks on their DSC thermograms (Figure 1) on the heating cycle. The compound with X = Ph showed a strong endotherm at 169°C and two weak endotherms at 190 and 216°C. And the *n*-C₄H₉O substituted compound exhibited a strong, low temperature endotherm at 128°C and two weak ones at 165 and 175°C. On the cooling DSC run they again showed the corresponding three exothermic peaks. The low temperature peaks are for crystal-to-mesophase 1 transitions and the higher temperature ones for mesophase 1-to-mesophase 2 and mesophase 2-to-isotropic phase transitions and vice versa. This was confirmed by microscopic observations of these compounds on a hot-stage as will be described below. One particular phenomenon observed for the compound with X = Ph was the occurrence of doublet type, low temperature peaks on the cooling DSC

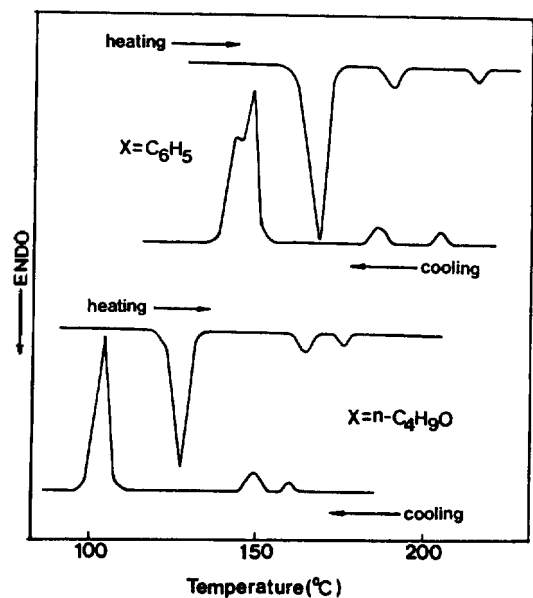


Figure 1. DSC thermograms of compounds 5 with $X = \text{C}_6\text{H}_5$ and $X = n\text{-C}_4\text{H}_9\text{O}$. The heating and cooling rate were $10^\circ\text{C}/\text{min}$.

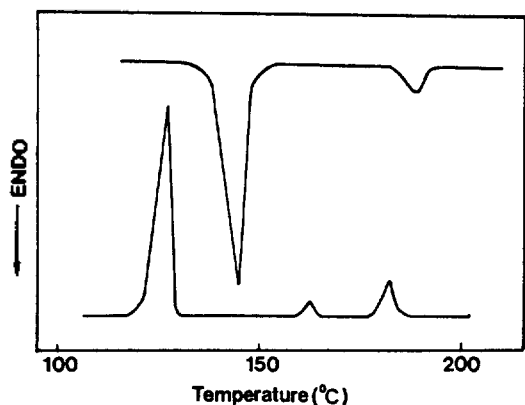


Figure 2. DSC thermogram of compound 5 with $X = \text{NO}_2$. The heating and cooling rate were $10^\circ\text{C}/\text{min}$.

curve. It is our present conjecture that the doublet crystallization exotherms came from two different crystal formations as observed earlier for others dimesogenic compounds.¹⁴ The compound with $X = \text{NO}_2$, on heating, revealed melting transition at 145°C and mesophase-to-isotropic transition at 190°C . It, however, exhibited monotropic behavior on cooling the isotropic phase as shown in Figure 2. Its cooling DSC thermogram showed isotropic-to-mesophase 2 transition at 183°C , mesophase 2-to-mesophase 1 transition at 163°C and finally solidification at 128°C . In contrast the rest of the compounds, *i.e.*, those with $X = \text{CN}$, Cl or H showed only melting transitions at 239 , 215 and 145°C , respectively, in the heating cycle. None of them was found to be even monotropic.

Nature of Mesophase. The thermal transitions observed by DSC analysis were further examined using a polarizing microscope equipped with a hot-stage. At the same time, the nature of mesophase formed by each compound were judged by their optical textures in the melts. All of the thermal transitions and transition temperatures described above coincided very well with microscopic observations.

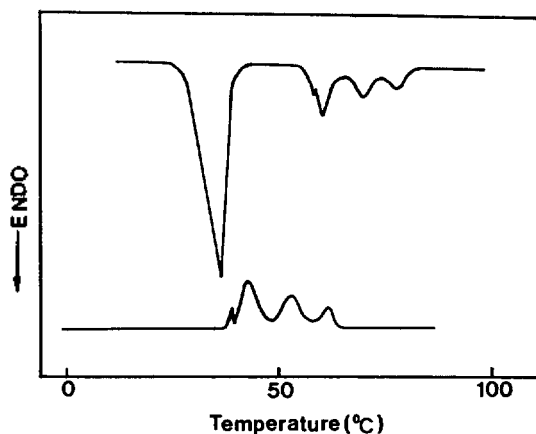


Figure 3. DSC thermogram of compound 6. The heating and cooling rate were $10^\circ\text{C}/\text{min}$.

According to the optical textures observed, the two compounds with $X = \text{Ph}$ and $n\text{-C}_4\text{H}_9\text{O}$ went through a series of transitions of crystal-to-smectic $A(S_A)$, smectic A -to-nematic(N) and nematic-to-isotropic phases and vice versa on heating or on cooling. In contrast, the NO_2 compound 5, upon heating, formed only a nematic phase on melting at 145°C and then exhibited nematic-to-isotropic phase transition at 214°C . On cooling its isotropic liquid, however, the compound went through nematic and thereafter S_A phases before the final solidification. In other words, this compound is capable of forming the S_A phase monotropically. The other three compounds with $X = \text{CN}$, Cl and H were not able to form any mesophase on heating as well as on cooling, *i.e.*, they are non-liquid crystalline.

Thermal transition behavior of the corresponding monomeric compounds 6 and 9 are in great comparison. For example, the compound 6 revealed five different endothermic peaks (Figure 3) at 35 , 59 , 59.9 , 69.5 and 77.7°C on the heating cycle of DSC analysis. The corresponding five peaks appeared also on the thermogram obtained from the cooling thermogram. The lowest temperature endothermic peak corresponds to crystal-to-smectic $B(S_B)$ transition and the rest to S_B -to- S_C , S_C -to- S_A , S_A -to-Nematic(N), N -to-isotropic phase transitions in that order. The thermal behavior of this compound was reported by Flannery and Haas¹¹, and by Smith *et al.*¹². There is, however, a significant discrepancy in their reported data. Our experimental results are practically the same as those by Flannery and Haas. They, however, did not provide the melting temperature of this compound, which we found is 35°C . On the contrary, all of the compounds 9, regardless of nature of the substituent X , exhibited reversibly only crystal-to-isotropic liquid transitions indicating that they are not mesomorphic. Therefore, the compounds 5 can be taken as those having a unique structural feature in that a polymorphic mesogen is linked through the hexamethylene spacer to a series of non-mesogenic rigid structures. And it is found that the mesophase they formed are much different from those formed by the mesogenic elements. In fact, as described above, some of them lost completely the mesophase-forming ability by the presence of non-mesogenic rigid units.

Thermodynamics of Phase Transitions. Table 3 summarizes not only the transition temperatures of the com-

Table 3. Thermal Transition of Compounds 5, 6 and 9

Compounds	T_m °C	T_{S_A-N} °C	T_{N-I} °C	ΔH_m KJ/mole	ΔH_{S_A-N} KJ/mole	ΔH_{N-I} KJ/mole
5(X = C ₆ H ₅)	169	190	216	30.2	3.6	1.3
5(X = <i>n</i> -C ₄ H ₉ O)	128	165	175	35.4	3.2	2.4
5(X = NO ₂)	145		190	53.5		3.5
	(128) ^a	(163) ^a	(183) ^a	(50.4) ^a	(2.3) ^a	(4.2) ^a
5(X = CN)	198			69.7		
5(X = Cl)	165			70.5		
5(X = H)	142			85.4		
6	35	59($T_{S_B-S_C}$) 59.9($T_{S_C-S_A}$) 69.5(T_{S_A-N})	77.7	13.7	0.43 ^b 2.54 ^b 1.01 ^b	0.72
9(X = C ₆ H ₅)	117			14.4		
9(X = <i>n</i> -C ₄ H ₉ O)	46			14.4		
9(X = NO ₂)	58			14.8		
9(X = CN)	62			15.8		
9(X = Cl)	51			13.1		
9(X = H)	41			18.8		

^a Values obtained from the cooling DSC curve. ^b These values are the ΔH values for the transitions of S_B-S_C , S_C-S_A , and S_A-N , respectively.

pounds, but also the enthalpy changes for the transitions obtained from the DSC analysis. The data for the monomeric compounds 6 and 9 also are included in the table. As far as the melting points are concerned, the *n*-C₄H₉O compound 5 having a relatively long and flexible alkoxy group has the lowest value (128 °C), whereas the compound 5 with a linear and highly polar C≡N group has the highest value (198 °C). Comparing the isotropization temperatures it is found that mesophase-stabilizing power of the substituent is in the order of Ph > NO₂ > *n*-C₄H₉O. This is in good agreement with the order of the nematic group efficiency observed for other series of monomesogenic and dimesogenic compounds.¹³

Now a question arises why the C≡N, Cl and H-substituted compounds are not liquid crystalline. This can at least partly ascribed to their high enthalpy changes for melting, ΔH_m , compared with those for the mesophase-forming compositions. According to the data given in Table 3 the value of ΔH_m for the non-liquid crystalline compounds range from about 70 to 85 KJ/mole, while those for the enantiotropically liquid crystalline compositions are significantly lower, 30–54 KJ/mole. The high value of ΔH_m would favor a direct phase transition from solid to the isotropic liquid phase owing to the fact that greater amount of thermal energy has to be provided for the transition. It also is very interesting to note that the ΔH_m value for the monotropic NO₂ compound lies in-between, 53.5 KJ/mole.

The monomeric compounds 6 and 9, as already described above, revealed quite different thermal behavior as compared with those of compounds 5. When thermal transitions of compounds 6 and 9 were observed on a cross-polarizing microscope, it was found that the compound 6 formed smectic B, smectic C, smectic A and then nematic phase before the final isotropization. None of the compounds 9 were able to form a mesophase in melts. The ΔH_m values of the monomeric compounds ranges from about 13 to 19 KJ/mole, which is substantially lower than those of 5. Lower molar

mass among others appears to be the main reason for the lower values.

All of the observations described up to this point strongly indicate that mesomorphic properties of the compounds 5 are quite distinct from those expected from a simple combination of the properties of the corresponding monomeric compounds 6 and 9. Especially, it should be noted that the compounds 5 with X = C≡N, Cl, or H are not liquid crystalline in spite of the fact that they all contain the mesomorphic structural moiety of the liquid crystalline compound 6.

Although we need more data on a wider range of compounds having the structure feature similar to the compounds 5 before we can draw any definite conclusion on correlation between their structure and liquid crystalline properties, it is fair to say that mesomorphic properties of a compound can not be predicted from a simple arithmetic coupling of the properties of structural elements it contains.

Conclusion

Mesomorphic properties of a series of new compounds consisting of a Schiff base type mesogenic group on one end connected through hexamethylene spacer to the *p*-substituted phenyl terephthaloyl structures on the other end, reveal that their liquid crystalline behavior is not a simple combination of the properties of the two terminal structural elements. In fact, the mesophases formed by a compound can not be predicted from the mesophases exhibited by the constituent, monomeric structures. Further work is deemed necessary to establish a more solid relationship between the structure and liquid crystalline properties having different mesophase-forming structural elements.

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CO₂ Laser Induced Decomposition of 1-Bromo-3-Chloropropane

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We have studied the Infrared Multiphoton Dissociation (IRMPD) of 1-bromo-3-chloropropane by using the pulsed CO₂ laser. The product yields and the HCl/HBr branching ratios in IRMPD of BrCH₂CH₂CH₂Cl are studied under the focused beam geometry as a function of buffer gas (He) pressure, laser energy, and photolysing wavelength. It is observed that the total dissociation yield has a laser energy dependence of 1.8-2.0 power order and the branching ratio is very slightly dependent on the pulse energy for the laser lines employed. The dependences of total dissociation yield and branching ratio on the buffer gas pressures show that the dissociation yield monotonically decreases and the branching ratio slightly decreases with the increase of the buffer gas pressure. The Energy-Grained Master Equation (EGME) was applied to explain the laser pulse energy and the buffer gas pressure(He) dependence of the dissociation yield and the branching ratio.

Introduction

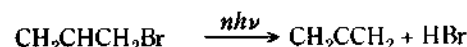
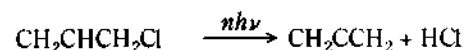
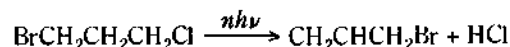
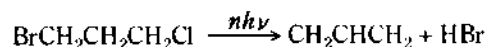
The infrared multiphoton dissociation(IRMPD) of polyatomic molecules with two or more dissociation channels has been an important subject for understanding of multiphoton absorption and decomposition process in the gas phase^{1,2}.

Molecular elimination reactions of halogenated compounds with competing reaction channels in the IRMPD has been reported by several workers^{1,3-9}. Halogenated compounds generally undergo unimolecular processes such as rearrangement, elimination and homolytic bond fission. Homolytic bond fission, relatively higher energy channel than molecular elimination, is preferred at a very high excitation energy level. It can be induced by highly intense IR laser¹⁰. Many workers have shown that the molecular elimination channel is generally more predominant in IRMPD of halogenated compounds^{1,4}.

The branching ratio of products can be varied by experimental conditions (fluence, pressure of buffer gases, beam geometry, laser frequency, and the number of pulses). Colussi *et al.*¹¹ reported that the HCl/DCl ratio in IRMPD of CH₂DCH₂Cl was independent of experimental conditions. However, it was generally observed that the branching ratio was affected by experimental parameters. Yano *et al.*³ reported that, in IRMPD of CF₂ClCH₂Cl, the branching ratio

of products (HF/HCl) decreased with the increase of the pulse energy, and increased with increasing the buffer gas pressure (Ar). Benson *et al.*⁴ also reported that the branching ratio (HCl/DCl) in the photolysis of CH₂DCH₂Cl decreased with increasing pressure in range of 0-5 torr and reached a plateau for pressures higher than 5 torr.

BrCH₂CH₂CH₂Cl may be considered to be decomposed *via* HBr and HCl molecular elimination followed by a secondary photolysis into allene.



The secondary photolysis has been recognized as a significant process in IRMPD, especially for the large molecules. It is, thus, necessary to study IRMPD of allyl chloride and allyl bromide, the primary dissociation products of BrCH₂CH₂CH₂Cl photolysis, in order to fully understand the IRMPD of BrCH₂CH₂CH₂Cl.

The irradiation zone becomes optically inhomogeneous