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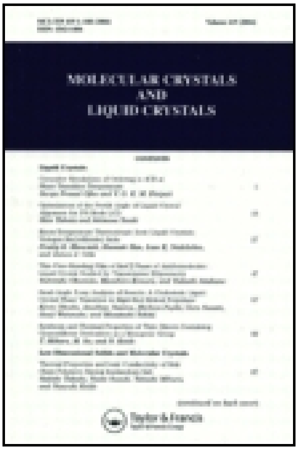

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Thermotropic Compounds with Two Terminal Mesogenic Units and a Central Spacer. 5[1]. Homologous Series of Polymethylene-α, ω-Bis (p-Oxybenzylidene Aniline)

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THERMOTROPIC COMPOUNDS WITH TWO TERMINAL MESOGENIC UNITS AND A CENTRAL SPACER. 5[1]. HOMOLOGOUS SERIES OF POLYMETHYLENE-α, ω-BIS(P-OXYBENZYLIDENE ANILINE)

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Two series of new thermotropic compounds with two terminal mesogenic units, p-oxybenzylidene-p-substituted anilines, attached to both ends of a central polymethylene spacer were prepared. The first series of compounds has central polymethylene spacers of varying length, while the second has different substituents on the aniline moiety of the mesogenic groups which are bracketing the central decamethylene spacer. The mesomorphic properties of the compounds were investigated by differential scanning calorimetry and on the hot-stage of a polarizing microscope. A thermodynamic analysis of the phase transitions of the compounds was made and the results are explained in relation to their structure.

1. INTRODUCTION

Among the many different types of nonamphiphilic liquid crystalline compounds[2-5], those of low molecular weight compounds consisting of two terminal mesogenic units attached to both ends of a central, flexible spacer have particularly interesting thermotropic properties. There are two main

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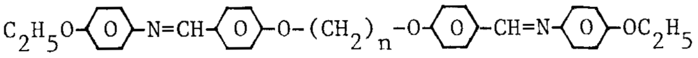
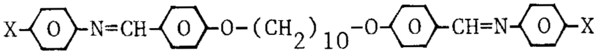
reasons for the growing interest in these compounds: one is the possible development of new liquid crystalline compounds with a wide mesophase temperature range, and the other is that the compounds may be taken as models for thermotropic, main chain polymers which contain mesogenic units interconnected through flexible spacers.

Recently we reported the synthesis and thermotropic properties of α, ω-bis(p-phenoxycarbonylphenoxy) alkanes[2] and α, ω-bis(4-nitrobenzoyloxyphenoxy) alkanes[3]. These compounds have aromatic-ester-type mesogenic units bracketing a central polymethylene spacer. The phase transition behavior of the compounds was strongly dependent on the nature of the terminal substituents and the length of the spacer.

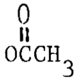
In the present investigation, in order to obtain further understanding of the structure-property relationship of liquid crystalline compounds, we have prepared two different series of compounds, Series I and II, shown below. Their thermal transitions and thermotropic properties were studied by differential scanning calorimetry (DSC) and on the hot-stage of a polarizing microscope. The structures and designation of the compounds are as follows:



Series I, n = 2-10 (I-2 - I -10)



Series II, X = H(II-H), CH_3(II-CH_3),OCH_3 (II-OCH_3), OC_2H_5(II-OC_2H_5), Br(II-Br), CN(II-CN), NO_2(II-NO_2), and



$\overset{O}{\overset{\|}{O}}CCH_3$ (II-O_2CCH_3).

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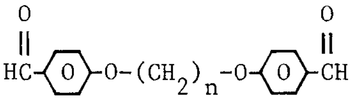
2. EXPERIMENTAL

2.1. Preparative Method

The compounds of Series I and II were prepared in two steps: the first step involved reacting p-hydroxybenzaldehyde with an α, ω-dibromoalkane in N,N-dimethylformamide in the presence of sodium carbonate, producing polymethylene-α, ω-bis-p-oxybenzaldehyde (I). In the second step, compound I was reacted with a p-substituted aniline in ethanol to obtain a Schiff-base-type product. Since an identical synthetic method was employed for the preparation of Series I and II compounds, only a representative method is given. Because II-O_2CCH_3 was synthesized in three steps, the third step used in its preparation is described in the next subsection, 2.2.



(I)

In a typical synthesis, 4-hydroxybenzaldehyde (6.1 g; 0.05 mole), 1,6-dibromohexane (6.1 g; 0.025 mole) and anhydrous sodium carbonate (6.6 g; 0.066 mole) were placed in a three-necked, round-bottomed flask equipped with a stirrer, nitrogen inlet and a water-cooled condenser. Dry N,N-dimethylformamide (14 mL) was mixed with the reactans in the flask. The reaction was conducted by refluxing the mixture under a nitrogen atmosphere for four hours. Afterwards, the reaction mixture was poured into 500 mL of water. The precipitate was collected by filtration and washed with water. After being dried, the crude product of hexamethylene-1,6-bis-p-oxybenzaldehyde, I, was recrystallized from absolute ethanol. The yield was 70 wt. %; the m.p.(110-111°C) of the compound was close to that reported in the literature[6].

A portion of product I thus obtained (2.28 g; 0.007 mole) and p-ethoxyaniline (1.92 g; 0.014 mole) were dissolved in 10 mL of ethanol in a three-necked, round-bottomed flask and the mixture refluxed for four hours under a nitrogen atmosphere. The mixture then was cooled to about 5°C and the precipitate collected by filtration.

TABLE I **The yields and results of elemental analysis of compounds I.**

Designation	Yield, wt. %	Elemental analysis, wt. %[a] C	H	N
I-2	76	75.11(75.57)	6.26(6.34)	5.13(5.51)
I-3	82	75.76(75.84)	6.55(6.56)	5.34(5.36)
I-4	80	76.05(76.09)	6.89(6.76)	4.96(5.22)
I-5	78	75.81(76.34)	7.11(6.96)	4.99(5.08)
I-6	72	76.60(76.57)	7.53(7.14)	4.68(4.96)
I-7	71	76.77(76.79)	7.54(7.31)	4.69(4.84)
I-8	73	77.09(77.00)	7.80(7.48)	4.65(4.72)
I-9	72	77.20(77.19)	7.89(7.64)	4.94(4.62)
I-10	83	77.35(77.38)	7.96(7.79)	4.42(4.51)

a. The values in the parentheses are theoretical ones.

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TABLE II The yields and results of elemental analysis of compounds II.

Designation	Yield, wt. %	Elemental analysis, wt. %[a]		
		C	H	N
II-H[b]	72	81.13(81.17)	7.69(7.57)	5.17(5.26)
II-CH_3[b]	78	81.49(81.43)	8.02(7.86)	4.88(4.99)
II-OCH_3[c]	82	76.85(76.99)	7.81(7.48)	4.76(4.73)
II-NO_2[c]	76	69.35(69.44)	6.14(6.15)	8.94(8.99)
II-CN[c]	73	78.52(78.35)	6.68(6.53)	9.39(9.62)
II-O_2CCH_3[c]	75	74.33(74.07)	6.98(6.79)	4.17(4.32)
II-OC_2H_5[c]	83	77.35(77.38)	7.96(7.79)	4.42(4.51)
II-Br[b]	80	62.50(62.62)	5.36(5.54)	3.90(4.06)

[a] The values in the parentheses are theoretical ones. II-Br was found to contain 25.38 wt. % Br. It's theoretical Br content is 23.19 wt. %.

[b] Compounds were recrystallized from chloroform.

[c] Compounds were recrystallized from toluene.

The precipitate was thoroughly washed with chilled 95% ethanol. The product, hexamethylene-1,6-bis(p-oxybenzylidene p-ethoxyaniline) (I-6), was recrystallized from toluene. The yield was 72 wt. % (Table I).

The structures of the series' intermediates, I, were confirmed by comparing their melting points with literature values, elemental analysis, and their IR(Perkin Elmer 710B) and NMR(Varian Associates EM 360A) spectra. The structures of the Series I and II products were verified by their IR spectra and elemental analysis (Tables I and II).

2.2. Preparation of Decamethylene-1, 10-bis(p-oxybenzylidene p-acetoxyaniline), II-O_2CCH_3

Decamethylene-1,10-bis(p-oxybenzylidene p-hydroxyaniline) (3.0 g; 0.005 mole), prepared by the same method as described above for the synthesis of compound I-6, was dissolved in a mixture of pyridine (10 mL) and acetic anhydride (1.09 g; 0.010 mole). The mixture was refluxed for two hours. After being cooled to room temperature, the mixture then was poured into 1 L of water. The precipitate was thoroughly washed with water. After being dried, the product, II-O_2CCH_3, was recrystallized from toluene. The yield was 75 wt. % and the m.p. of the compound was 161°C.

2.3. Study of the Thermal and Optical Properties of the Compounds

The thermal behavior of each compound was studied on a du Pont 910 DSC instrument. The DSC thermograms were obtained under a nitrogen atmosphere at heating and cooling rates of 10°C/min. Phase transitions also were observed visually, both on heating and cooling, using an ordinary capillary melting point apparatus. Thermodynamic parameters for the phase transitions were obtained from the areas of transition peaks on the DSC thermograms, indium being used as the standard for calibration. Optical textures of the melts and thermal behavior of the compounds were further examined on the hot-stage(Mettler FP-5) of a polarizing microscope (Leitz, Orthoplan).

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3. RESULTS AND DISCUSSION

3.1. Synthesis and Identification of the Compounds

The yields and results of elemental analyses of the Series I and II compounds are given in Tables I and II. The yields reported in the tables are for the final steps, from the corresponding polymethylene-α, ω-bis(p-oxybenzaldehyde) (I) to the products. The yields are,in general, 70-80 wt. % after recrystallization. The results of the compounds' elemental analyses are in good agreement with calculated values. Their structures were further confirmed by their IR spectra. All of the compounds exhibited relatively strong IR absorptions at about 1620 Cm^{-1} for the $>$C=N- stretching vibration and around 1160 Cm^{-1} for the $-\overset{|}{\underset{|}{C}}-O-Ar$ bending vibration.

3.2. Mesomorphic Properties of the Compounds of Series I

In this series, the length of the central polymethylene spacer was varied and its effect on the thermal and liquid crystal properties of the compounds was studied. All of the compounds of Series I reversibly exhibited two transitions, one for melting and the other for the transition from nematic to isotropic phases, both on the heating and the cooling cycle of the DSC analysis. They formed nematic phases upon melting. This was determined by their Schlieren textures observed on the hot-stage of a polarizing microscope. DSC analysis and microscopic observation of the phase transitions showed that the nematic phases were enantiotropically formed.

The transition temperatures for melting (Tm) and those for nematic phase to isotropic liquid (Ti), recorded in

TABLE III Thermodynamic data of Series I compounds.

Designation	Tm, °C	Ti, °C	ΔT, °C	ΔHm, KJ/mole	ΔHi, KJ/mole	ΔSi, J/mole·°K	ΔHi/ΔHm, %
I-2	233	285	52	49.7	7.4	13.2	14.8
I-3	175	186	11	38.3	2.1	4.4	5.4
I-4	216	263	47	44.4	6.9	12.9	15.4
I-5	183	200	17	38.2	2.2	4.7	5.8
I-6	205	235	30	57.7	6.7	13.1	11.5
I-7	169	196	27	43.9	3.3	7.0	7.4
I-8	196	216	20	55.7	6.4	13.1	11.5
I-9	161	187	26	47.6	3.5	7.6	7.4
I-10	190	202	12	67.4	5.8	12.3	8.6

Table 3, were obtained from the heating cycles of the DSC analyses and are represented in Figure 1. The values of both Tm and Ti tend to decrease in a regular, zig-zag fashion with the length, n, of the central polymethylene spacer. Such a pattern of regular change has often been observed in compounds consisting of central mesogenic structures having varying lengths of terminal alkyl groups[4,7,8].

Even though their crystal structures are not known, it is reasonable to assume that having an even-numbered polymethylene spacer favors a more efficient packing of the molecules in the crystal lattice, as observed in n-paraffins. This may be the reason why the compounds with even-numbered

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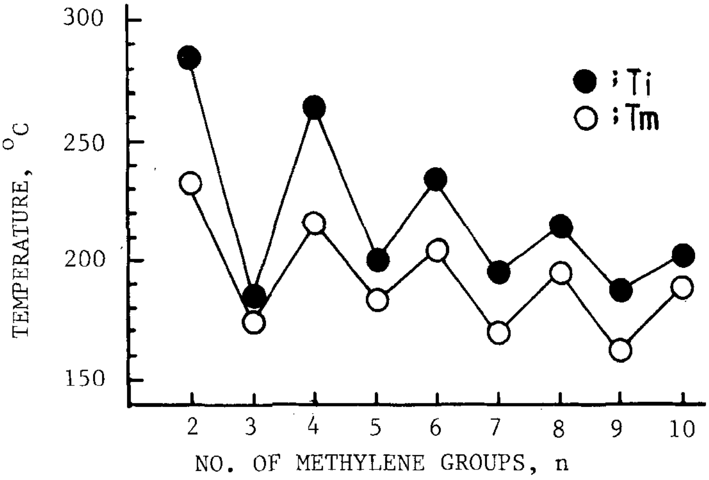

FIGURE 1 Dependence of Tm and Ti of the compounds of Series I on the length, n, of polymethylene spacer

polymethylene spacers have higher Tm's than those with odd-numbered ones. It should be pointed out, however, that many other homologous series exist which show irregular changes in melting points with alkyl chain length[9].

In addition to the regular, zig-zag decrease, a diminishing amplitude between the Ti's of the even- and odd-numbered polymethylene spacers is observed as the spacer grows in length. The exact same trend was reported earlier for Ti values of 4-p-n-alkoxybenzylidene aminobiphenyls[10] and other homologous series[8,9]. The regular decrease in Ti's can be interpreted as the regular change in the anisotropy of molecular polarizability on passing from even to odd polymethylene chains, or vice versa[11]. Other explanations for this alternation are also possible[11]. The observed diminished change with the length of polymethylene

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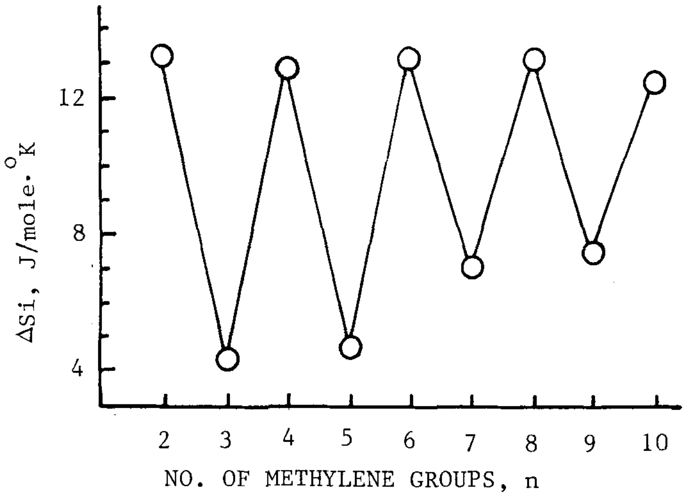

FIGURE 2 Dependence of ΔSi of the compounds of Series I on the length, n, of the polymethylene spacer

spacer may be due to an increased probability of adopting conformational variations by the methylene groups. Figure 1 also shows that, in even-numbered spacers, the mesophase temperature range (ΔT) decreases with increasing length of the central polymethylene group, while in odd-numbered spacers, the ΔT seems to increase with increasing size. Unfortunately, the reason for such difference is not yet clear. It is also pointed out that the ΔT's of the present compounds do not seem to be wider than those of compounds having only one mesogenic group.

Figure 2 illustrates the dependence of ΔSi, the entropy change for the transition from nematic to isotropic phases, on the length and on the number (odd or even) of methylene units in the central spacer. The magnitude of ΔSi for the compounds with even-numbered polymethylene

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spacers is consistently greater than those with odd-numbered ones. The amplitude of the alternation seems to decrease slightly as the length of the spacer increases. This phenomenon can be taken as a suggestion that the mesophase of the compounds having even-numbered polymethylene units is of a higher degree of order at Ti than those with odd-numbered ones. Similar trends were repeatedly observed for other series of homologous compounds[2,3,12-14].

For the relatively short spacers, the methylene groups are most likely to exhibit an anti or trans conformation[15]. This would allow for the two terminal mesogenic units to be more or less colinear in the compounds with even-numbered methylene units. On the other hand, the two terminal mesogenic groups would be out of line and form a bent angle when there are an odd number of methylene structures in the central spacer. Therefore, the former would result in a mesophase with a higher degree of order than the latter. Chang et al.[16] earlier measured order parameters at Ti of p-alkoxybenzylidene-p-n-butylanilines and found that the values for the compounds with alkoxy groups consisting of an even number of carbon atoms were consistently higher than those for compounds with an odd number of carbons in the chain.

Another fact to be pointed out is that the magnitude of ΔSi of the present compounds is significantly greater than those of other nematic compounds having only one mesogenic group. The last column of Table 3 shows that enthalpy change (ΔHi) for the nematic to isotropic transition of the compounds ranges from 5-15% of the heat of fusion (ΔHm). This percentage of ΔHi with respect to ΔHm is about twice that of other common nematic compounds with

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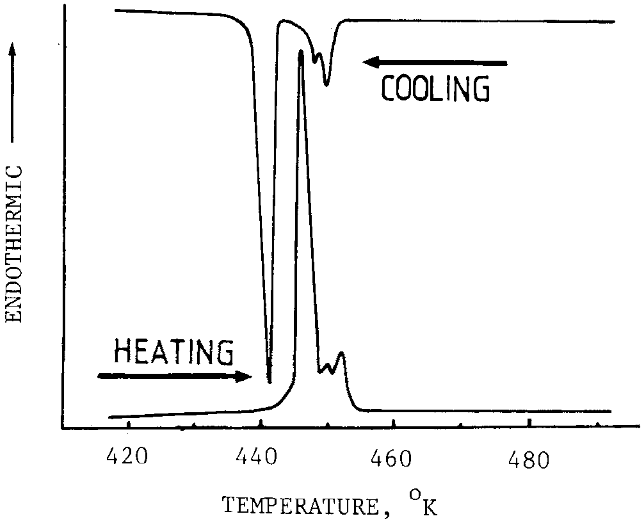

FIGURE 3 DSC thermogram of the compound II-Br. Heating and cooling rates were 10°C/min.

one mesogenic unit[17]. Similar observations were previously reported by us[2,3] for compounds having aromatic-ester-type mesogenic groups attached to both ends of the polymethylene spacers.

3.3. Mesomorphic Properties of the Compounds of Series II

The effect on the thermal and thermotropic properties of the compounds of terminal substituents, H, CH_3, OCH_3, OC_2H_5, Br, CN, NO_2 and O_2CCH_3, attached to both mesogenic units was investigated in this series. The central spacer was fixed as decamethylene.

All of the compounds of this series, with the exception of II-H, were thermotropic. The compounds II-CH_3 and II-OCH_3 were monotropic, while the rest were enantiotropic. II-Br showed a three-step transition of solid→smectic A→

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nematic → isotropic phase (see Figure 3). In contrast, the other compounds exhibited only two transitions, solid → nematic → isotropic liquid. The data of thermal transitions and thermodynamic parameters are recorded in Table 4. If we judge the nematic group efficiency of the substituents by Ti's of the compounds, the following order is obtained: $C_2H_5O \geq CH_3COO \geq CN > Br \geq NO_2$. This order is only in fair agreement with those of other series of thermotropic compounds[18].

As one can see from Table 4, the value of ΔHm of II-OCH_3 is significantly higher than those of the other compounds,

TABLE IV Thermodynamic data of Series II compounds.[a]

Designation	Tm, °C	Ti, °C	ΔHm, KJ/mole	ΔHi, KJ/mole	ΔSi, J/mole•°K	ΔHi/ΔHm, %
II-H	153	-	59.1	-	-	-
II-CH_3	164	-	65.3			
	(141)	(161)	(65.8)	(3.7)	(8.4)	(5.9)
II-OCH_3	199	-	94.4			
	(167)	(189)	(92.2)	(4.5)	(9.7)	(4.8)
II-NO_2	149	179	56.5	5.0	11.0	8.0
II-CN	151	200	42.6	5.1	10.8	12.0
II-O_2CCH_3	161	201	55.1	5.5	11.5	9.9
II-OC_2H_5	190	202	67.4	5.8	12.3	8.6
II-Br[b]	172	177	43.3	4.2	9.4	9.8
		180		4.9	10.7	11.3

[a] The values in parentheses are the ones obtained from the cooling cycles of DSC analysis.

[b] The top values are for smetic A-to-nematic phase transition and the bottom ones are for nematic-to-isotropic phase transition.

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which may be the reason for the monotropic nature of the compound. The fact that II-H is non-liquid crystalline tells us that H is a very poor nematogenic substituent, as expected. Here again, the magnitude of ΔSi and the ratios of ΔHi/ΔHm of the compounds are much greater than other types of liquid crystalline compounds consisting of only one mesogenic unit[17]. The possible reasons for the observation given above for the Series I compounds should hold true also for the present series.

4. CONCLUSION

The synthesis of the new compounds of Series I and II has been described. All of the compounds have two identical mesogenic units, p-oxybenzylidene-p-substituted anilines, attached to either end of a central polymethylene spacer. The Series I compounds were all enantiotropically nematic and revealed that both Tm and Ti decrease in a zig-zag fashion as the number of methylene units in the spacer increases. The compounds with an even number of methylene groups in the spacer showed higher values of ΔSi than those with an odd number, indicating that the mesophases of the even-numbered compounds at Ti are of a higher degree of order than those of the odd-numbered ones.

The Ti's of the compounds of Series II suggest the nematic group efficiency of $C_2H_5O \geq CH_3COO \geq CN > Br \geq NO_2$. Compound II-H was non-liquid crystalline and II-CH_3 and II-OCH_3 were monotropic. The others were enantiotropic and nematic. Compound II-Br was the only one which could form an S_A phase as well as a nematic phase before clearing. All of the present mesomorphic compounds exhibit greater values of ΔSi and ΔHi/ΔHm compared to compounds having only one mesogenic unit.

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