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PHASE TRANSITIONS IN MESOMORPHIC *p,p'*-DIALKOXY-SUBSTITUTED BENZYLIDENE-ANILINES

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ABSTRACT

The transition temperatures for the mesomorphic homologous series of *p-n*-alkoxy-benzylidene-*p'*-pentyloxyanilines and *p-n*-alkoxy-benzylidene-*p'*-esiloxy-anilines obtained by thermal microscopy are reported. The transition diagrams are briefly discussed.

INTRODUCTION

Sixteen compounds of general formula

$H_{11}C_5—O—C_6H_4—N{=}CH—C_6H_4—O—C_nH_{2n+1}$ (series I)

and

$H_{13}C_6—O—C_6H_4—N{=}CH—C_6H_4—O—C_nH_{2n+1}$ (series II)

with $n = 1, 2, \cdots 8$ (compounds 1–8 and 9–16, respectively), have been synthesized using the standard method reported previously [1]. Their phase behaviour on heating and on cooling has been studied, and the thermal cycles for all the compounds are reported in the present work.

EXPERIMENTAL

Materials

Commercially available amines and aldehydes were used for the synthesis of the compounds. Equivalent quantities of amine and aldehyde were dissolved in anhydrous benzene, and refluxed for 4–5 h. The water of reaction was removed azeotropically and the product yield was about 80%. In every case the crude products were purified by several crystallizations at low temperature from anhydrous ethanol at constant melting point.

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Thermal microscopy (TM)

The transition temperatures were observed using a Galileo polarizing microscope with a 20 × 0.22 objective, and a Mettler FP 52 microfurnace for sample temperature control. Samples were mounted on a glass slide and covered with a glass cover slip. Special care was taken to ensure clear observation.

RESULTS AND DISCUSSION

Tables 1 and 2 report the transition diagrams for the two series of compounds. The transition temperatures for all the compounds were determined from several TM runs (a minimum of four). All data were taken at scan rates of 2°C min^{-1}. On account of the effect of purity on the transition temperature [2], particular attention was paid to purification of

TABLE 1

Transition diagrams for compounds 1–8

1

$$\begin{tikzcd}
K \arrow[rr, "68.8^\circ C"] & & I.L. \arrow[dl, "59.4^\circ C"] \\
& N \arrow[ul] &
\end{tikzcd}$$

2 $K \underset{92^\circ C}{\overset{94.3^\circ C}{\rightleftarrows}} N \underset{120.9^\circ C}{\overset{121^\circ C}{\rightleftarrows}} I.L.$

3 $K \underset{104^\circ C}{\overset{105.8^\circ C}{\rightleftarrows}} N \underset{106.8^\circ C}{\overset{107.2^\circ C}{\rightleftarrows}} I.L.$

4

$$\begin{tikzcd}
K \arrow[rr, "115.7^\circ C"] & & I.L. \arrow[dl, "114.7^\circ C"] \\
& N \arrow[ul] &
\end{tikzcd}$$

5

$$\begin{tikzcd}
K \arrow[rr, "113.2^\circ C"] & & I.L. \arrow[dl, "108.2^\circ C"] \\
& N \arrow[ul] &
\end{tikzcd}$$

6 $K \underset{100.1^\circ C}{\overset{103.6^\circ C}{\rightleftarrows}} N \underset{112.2^\circ C}{\overset{112.5^\circ C}{\rightleftarrows}} I.L.$

7 $K_1 \overset{90.8^\circ C}{\rightleftarrows} K_2 \underset{93.5^\circ C}{\overset{93.8^\circ C}{\rightleftarrows}} S \underset{98.3^\circ C}{\overset{98.5^\circ C}{\rightleftarrows}} N \underset{109.5^\circ C}{\overset{109.6^\circ C}{\rightleftarrows}} I.L.$

8

$$\begin{tikzcd}
K \arrow[r, "89.2^\circ C"] & S \arrow[r, shift left, "101.8"] \arrow[d, "88^\circ C"] & N \arrow[l, shift left, "101.6"] \arrow[r, shift left, "110.8^\circ C"] & I.L. \arrow[l, shift left, "110.6^\circ C"] \\
S \arrow[u, "\sim 79^\circ C"] & S \arrow[l, "82^\circ C"] & &
\end{tikzcd}$$

K, Solid; N, nematic; S, smectic; I.L., isotropic liquid.

TABLE 2

Transition diagrams for compounds 9–16

9	$\begin{tikzcd} K \arrow[rr, "105^{\circ}\mathrm{C}"] & & \mathrm{I.L.} \arrow[dl, "103.1^{\circ}\mathrm{C}"] \\ & N \arrow[ul] & \end{tikzcd}$
10	$K_1 \rightleftarrows K_2 \underset{89.8^{\circ}\mathrm{C}}{\overset{102.2^{\circ}\mathrm{C}}{\rightleftarrows}} N \underset{123.3^{\circ}\mathrm{C}}{\overset{123.4^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{I.L.}$
11	$K_1 \rightleftarrows K_2 \overset{101.7^{\circ}\mathrm{C}}{\rightleftarrows} N \underset{109.4^{\circ}\mathrm{C}}{\overset{109.7^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{I.L.}$
12	$K \underset{101^{\circ}\mathrm{C}}{\overset{103.5^{\circ}\mathrm{C}}{\rightleftarrows}} N \underset{117.4^{\circ}\mathrm{C}}{\overset{117.7^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{I.L.}$
13	$K \underset{102^{\circ}\mathrm{C}}{\overset{104.7^{\circ}\mathrm{C}}{\rightleftarrows}} N \underset{111.5^{\circ}\mathrm{C}}{\overset{111.7^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{I.L.}$
14	$K \underset{105.5^{\circ}\mathrm{C}}{\overset{107^{\circ}\mathrm{C}}{\rightleftarrows}} N \underset{115.2^{\circ}\mathrm{C}}{\overset{116^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{I.L.}$
15	$K \overset{101^{\circ}\mathrm{C}}{\rightleftarrows} S \underset{102.5^{\circ}\mathrm{C}}{\overset{102.8^{\circ}\mathrm{C}}{\rightleftarrows}} N \underset{112.4^{\circ}\mathrm{C}}{\overset{113.3^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{I.L.}$
16	$\begin{tikzcd} K \arrow[rr, "93.7^{\circ}\mathrm{C}"] & & S_1 \arrow[dl, "91^{\circ}\mathrm{C}"] \arrow[r, shift left, "107.3^{\circ}\mathrm{C}"] & N \arrow[l, shift left, "107.3^{\circ}\mathrm{C}"] \arrow[r, shift left, "114.8^{\circ}\mathrm{C}"] & \mathrm{I.L.} \arrow[l, shift left, "114.5^{\circ}\mathrm{C}"] \\ & S_2 \arrow[ul] & & & \end{tikzcd}$

K, Solid; N, nematic; S, smectic; I.L., isotropic liquid.

the products. Data on the monotropic mesophases of the compounds were obtained as follows. The samples were heated from solid to isotropic liquid, then cooled until formation of the mesophase but without formation of the solid phase. The mesophases so obtained were reheated under the same experimental conditions to the isotropic liquid. The samples were then cooled until the solid phase was again obtained. Thermal data concerning compound 5 have been reported by Weigand and Gabler [3].

From an evaluation of the experimental data it can be seen that there are four different kinds of thermal cycle: one with only a monotropic nematic transition—compounds 1, 4, 5 and 9; one with only a nematic stable phase —compounds 2, 3, 6, 10, 11, 12, 13 and 14; one which presents, besides a stable nematic phase, a smectic stable phase—compounds 7 and 15; and one which is more complicated than the other three which also produces smectic monotropic phases—compounds 8 and 16.

Figures 1 and 2 plot the trends of the transition temperatures for the compounds under study. As suggested in ref. 4 the random nature of the crystal-to-mesophase transition temperature within a homologous series can be attributed to the wide variety of possible crystal structures.

Compounds 7, 10 and 11 show already at room temperature at least two different solid phases before melting. An X-ray study of the *p*-alkoxy-ben-

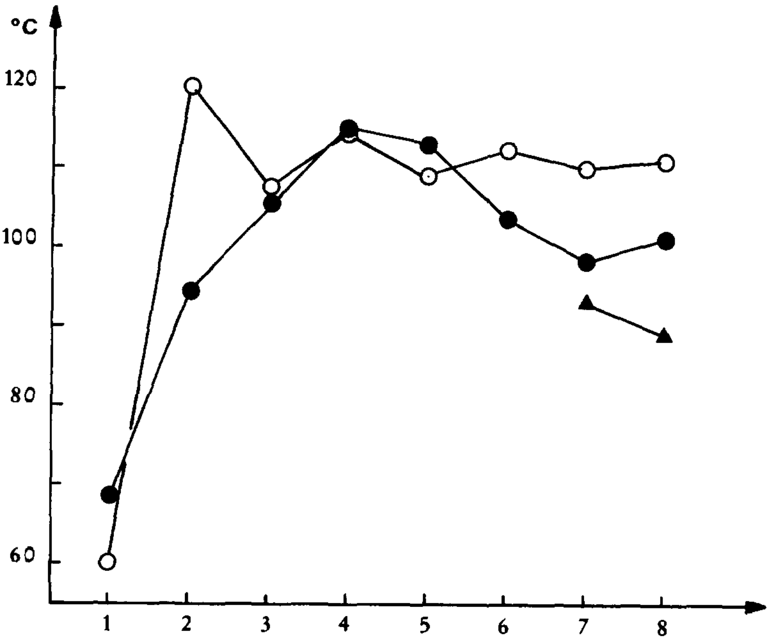

Fig. 1. Effect of alkyl chain length on the transition temperatures (series I). ●, Crystal → nematic or isotropic; ○, nematic → isotropic; ▲, smectic → nematic.

zoic acids [5] revealed no similarities in crystal structure for the lower homologues; however from *p*-*n*-heptyloxybenzoic acids onwards a similarity was observed. These results are reflected in the crystal-to-mesophase transi-

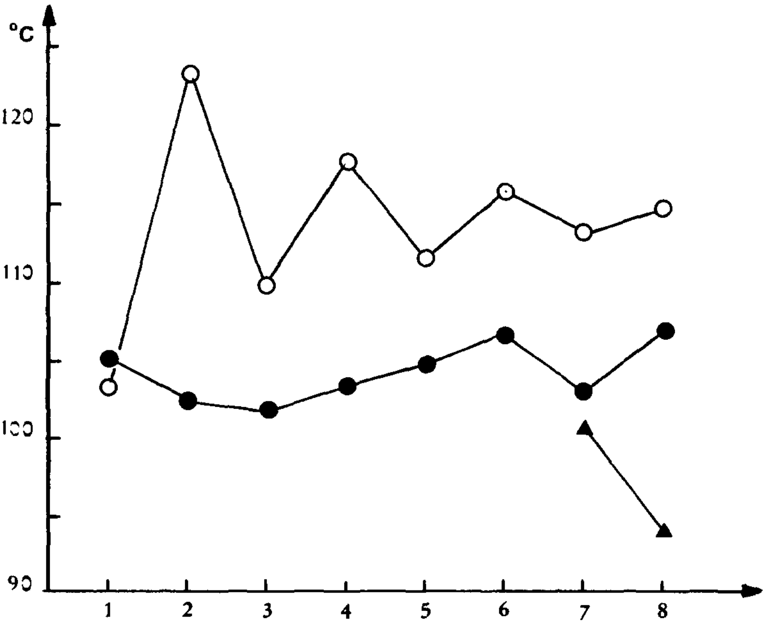

Fig. 2. Effect of alkyl chain length on the transition temperatures (series II). ●, Crystal → nematic or isotopic; ○, nematic → isotropic; ▲, smectic → nematic.

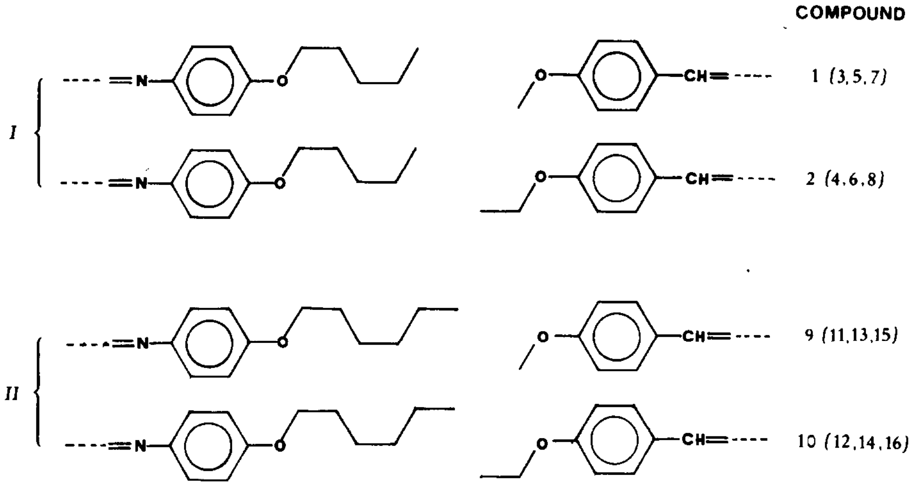

Fig. 3. Terminal situation of neighbouring molecules.

tion temperatures [6], which change from a random to an even–odd alternation starting with the *p*-*n*-heptyloxy derivative. The trends of clearing temperatures against the number of carbon atoms in the alkyl chain show the characteristic even–odd effect as expected for molecules of this kind [7]. Nevertheless, from a comparison of Figs. 1 and 2 little increase in mesomorphic thermal stability of the second series of compounds with respect to the corresponding compounds of the first series is observed. Moreover, for the second series of compounds, except compound 9, the nematic phase is stable over a large temperature range. This behaviour is in contrast with those shown by the first series of compounds reported here and by the two homologous series reported in ref. 1, which have shorter molecules. If we refer to the simple molecular scheme reported in Fig. 3, it is seen that for the second series of compounds the terminal situation of neighbouring molecules makes the interaction between the adjacent tails easy. In particular, compounds 10, 12, 14 and 16 with terminal bonds lying on the same axis show greatest clarification temperatures together with great stability of the mesophases. In this situation the tail–tail interactions are favoured.

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