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PHASE TRANSITIONS IN MESOMORPHIC BENZYLIDENE-ANILINES

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ABSTRACT

The transition temperatures for the mesomorphic homologous series of *p*-*n*-alkoxy-benzylidene-*p*′-propoxy-anilines, and *p*-*n*-alkoxy-benzylidene-*p*′-butoxy-anilines are presented. The transition diagrams are briefly discussed.

INTRODUCTION

As a continuation of our work [1] concerning the liquid crystalline properties of Schiff bases, we have synthesized two series of compounds of general formula

$$H_7C_3O{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}OC_nH_{2n+1} \qquad \text{(series I)}$$

and

$$H_9C_4O{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}OC_nH_{2n+1} \qquad \text{(series II)}$$

with $n = 1, 2, \ldots, 8$ (compounds 1–8 and 9–16, respectively). The phase behaviour of these compounds was studied by means of thermal microscopy (TM).

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.

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

On account of the effect of purity on the transition temperature [2], particular attention was paid to purification of the products. Tables 1 and 2 report the transition diagrams for the two series of compounds. The transition temperatures reported are the averages of several measurements.

TABLE 1

Transition diagrams

1

$$\begin{tikzcd}
K \arrow[rr, "119^\circ C"] & & I.L. \arrow[dl, shift left] \\
& N \arrow[ul, "96^\circ C"] \arrow[ur, shift left, "96^\circ C"'] &
\end{tikzcd}$$

2

$$\begin{tikzcd}
K_1 \arrow[r, shift left, "126^\circ C"] & K_2 \arrow[l, shift left] \arrow[rr, "127.4^\circ C"] & & I.L. \arrow[dl, shift left, "125.2^\circ C"] \\
& & N \arrow[ul, "114^\circ C"] \arrow[ur, shift left, "125.2^\circ C"] &
\end{tikzcd}$$

3

$$\begin{tikzcd}
K_1 \arrow[r, shift left, "282^\circ C"] & K_2 \arrow[l, shift left] \arrow[r, shift left, "135^\circ C"] & I.L. \arrow[l, shift left, "115^\circ C"]
\end{tikzcd}$$

4

$$\begin{tikzcd}
K_1 \arrow[r, shift left, "79^\circ C"] & K_2 \arrow[l, shift left] \arrow[rr, "120.5^\circ C"] & & I.L. \arrow[dl, shift left, "114.7^\circ C"] \\
& & N \arrow[ul, "108^\circ C"] \arrow[ur, shift left, "114.5^\circ C"] &
\end{tikzcd}$$

5

$$K \underset{100^\circ C}{\overset{104.4^\circ C}{\rightleftarrows}} N \underset{106.1^\circ C}{\overset{106.2^\circ C}{\rightleftarrows}} I.L.$$

6

$$K \underset{92^\circ C}{\overset{99^\circ C}{\rightleftarrows}} N \underset{110.5^\circ C}{\overset{110.5^\circ C}{\rightleftarrows}} I.L.$$

7

$$K \underset{92^\circ C}{\overset{102^\circ C}{\rightleftarrows}} N \underset{107^\circ C}{\overset{107.2^\circ C}{\rightleftarrows}} I.L.$$

8

$$K \underset{90.3^\circ C}{\overset{99.6^\circ C}{\rightleftarrows}} N \underset{108.9^\circ C}{\overset{109^\circ C}{\rightleftarrows}} I.L.$$

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

TABLE 2

Transition diagrams

9
$$\begin{tikzcd}
K \arrow[rr, "114.5^{\circ}\mathrm{C}"] & & \mathrm{I.L.} \arrow[dl, shift left, "108.3^{\circ}\mathrm{C}"'] \\
& N \arrow[ul, "99^{\circ}\mathrm{C}"] \arrow[ur, shift left, "108.4^{\circ}\mathrm{C}"'] &
\end{tikzcd}$$

10
$$\begin{tikzcd}
K \arrow[r, shift left, "111.8^{\circ}\mathrm{C}"] & N \arrow[l, shift left, "95^{\circ}\mathrm{C}"] \arrow[r, shift left, "132.8^{\circ}\mathrm{C}"] & \mathrm{I.L.} \arrow[l, shift left, "132.5^{\circ}\mathrm{C}"]
\end{tikzcd}$$

11
$$\begin{tikzcd}
K \arrow[rr, "120.6^{\circ}\mathrm{C}"] & & \mathrm{I.L.} \arrow[dl, shift left, "114.9^{\circ}\mathrm{C}"'] \\
& N \arrow[ul, "105^{\circ}\mathrm{C}"] \arrow[ur, shift left, "115^{\circ}\mathrm{C}"'] &
\end{tikzcd}$$

12
$$\begin{tikzcd}
K \arrow[rr, "125.5^{\circ}\mathrm{C}"] & & \mathrm{I.L.} \arrow[dl, shift left, "122.5^{\circ}\mathrm{C}"'] \\
& N \arrow[ul, "110^{\circ}\mathrm{C}"] \arrow[ur, shift left, "122.7^{\circ}\mathrm{C}"'] &
\end{tikzcd}$$

13
$$\begin{tikzcd}
K \arrow[rr, "115.6^{\circ}\mathrm{C}"] & & \mathrm{I.L.} \arrow[dl, shift left, "114.5^{\circ}\mathrm{C}"'] \\
& N \arrow[ul, "109^{\circ}\mathrm{C}"] \arrow[ur, shift left, "114.7^{\circ}\mathrm{C}"'] &
\end{tikzcd}$$

14
$$\begin{tikzcd}
K \arrow[r, shift left, "101.2^{\circ}\mathrm{C}"] & N \arrow[l, shift left, "98^{\circ}\mathrm{C}"] \arrow[r, shift left, "117.7^{\circ}\mathrm{C}"] & \mathrm{I.L.} \arrow[l, shift left, "117.5^{\circ}\mathrm{C}"]
\end{tikzcd}$$

15
$$\begin{tikzcd}
K \arrow[r, shift left, "99.8^{\circ}\mathrm{C}"] & S_1 \arrow[l, shift left, "98.4^{\circ}\mathrm{C}"] \arrow[r, "101.6^{\circ}\mathrm{C}"] & N \arrow[r, shift left, "113.9^{\circ}\mathrm{C}"] \arrow[d, shift right, "95.8^{\circ}\mathrm{C}"'] & \mathrm{I.L.} \arrow[l, shift left, "113.8^{\circ}\mathrm{C}"] \\
& S_2 \arrow[ul, "99.5^{\circ}\mathrm{C}"'] \arrow[u] \arrow[r, shift left, "94.4^{\circ}\mathrm{C}"] & S_3 \arrow[l, shift left, "94.5^{\circ}\mathrm{C}"] \arrow[u, shift right, "95.3^{\circ}\mathrm{C}"'] &
\end{tikzcd}$$

16
$$\begin{tikzcd}
K \arrow[rr, "108.6^{\circ}\mathrm{C}"] & & N \arrow[r, shift left, "114.8^{\circ}\mathrm{C}"] \arrow[dl, shift left, "99.4^{\circ}\mathrm{C}"'] & \mathrm{I.L.} \arrow[l, shift left, "114.7^{\circ}\mathrm{C}"] \\
& S \arrow[ul, "88^{\circ}\mathrm{C}"] \arrow[ur, shift left, "99.8^{\circ}\mathrm{C}"'] & &
\end{tikzcd}$$

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

Data on the monotropic mesophases of the compounds were obtained as follows. The samples were heated from solid to isotropic liquid at 2°C min^{-1}. The isotropic liquid was then cooled at the same rate until the mesophase was formed, but the solid phase had not formed. The mesophases so obtained were reheated under the same experimental conditions to the isotropic liquid. The sample was then cooled until the solid phase was again obtained. Some of the mesomorphic benzylidene-anilines reported here have been described previously [3]. Where a comparison is possible, good agreement exists between our results and literature data. However, the clearing temperature (T_c) for compound 3 observed in the present experiment and in agreement with that reported in ref. 4, is different from that (108°C) reported in ref. 5. Moreover, great attention was paid to the determination of the transition diagram of this compound because, as reported in Table 1, no nematic phase is evident, in contrast with the literature data [4]. The solid–solid transitions evident in the diagrams of compounds 2, 3 and 4 may be confirmed by means of the differential scanning calorimetry (DSC) measurements now in progress.

From an evaluation of the experimental data it is observed that compounds 1, 2, 4, 9, 11, 12 and 13 show a similar thermal behaviour characterized by a nematic monotropic transition, while compounds 5, 6, 7, 8, 10 and 14 give a stable nematic phase. On cooling, compound 16 shows a smectic monotropic phase which solidifies at about 88°C. Lastly, compound 15 shows a very complicated diagram: on cooling the nematic phase, at least two smectic monotropic phases are detectable by TM, the second of which (the smectic phase at lowest temperature) gives alternatively a solid or a stable smectic phase, the latter at 99.5°C.

A study by means of DSC and X-ray techniques in order to characterize the cited smectic phases for compounds 15 and 16 will be carried out as soon as possible.

Figures 1 and 2 plot the trends of the transition temperatures for the compounds under study. As suggested in ref. 6, the random nature of the crystal-to-mesophase transformation within a homologous series can be

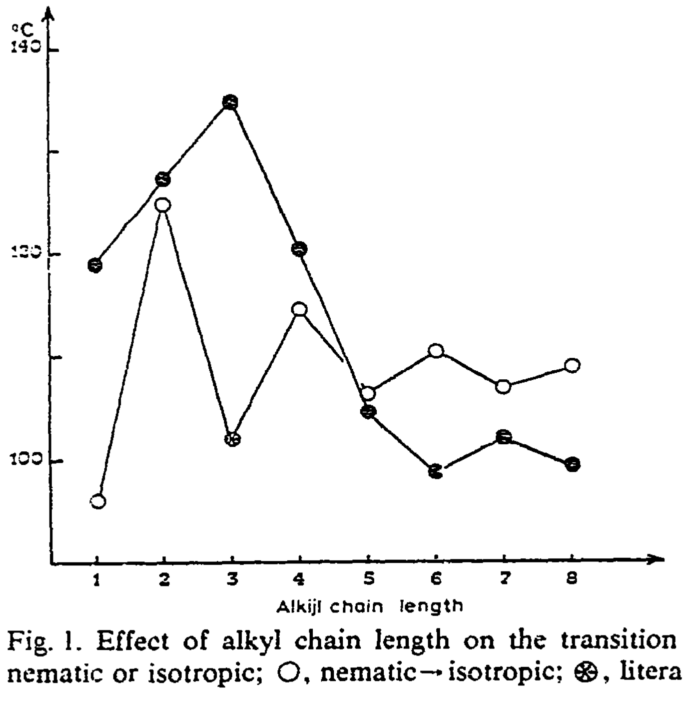

Fig. 1. Effect of alkyl chain length on the transition temperatures (series I). ●, Crystal→ nematic or isotropic; ○, nematic→isotropic; ⊗, literature datum.

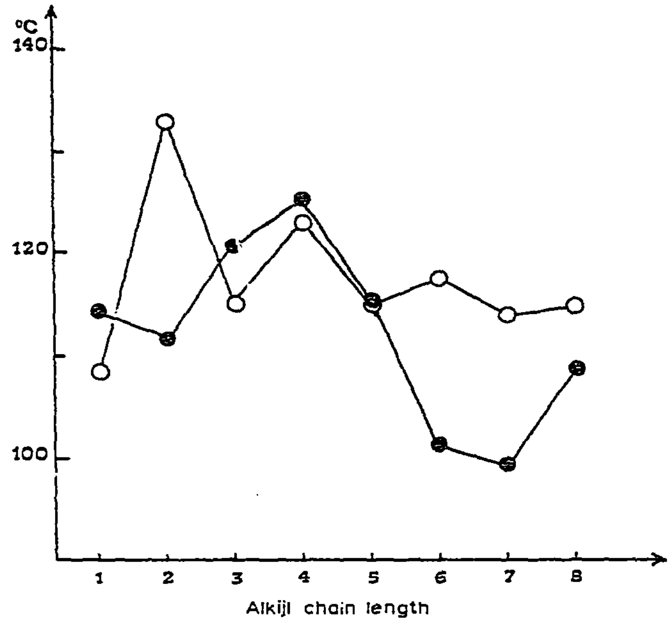

Fig. 2. Effect of alkyl chain length on the transition temperatures (series II). ●, Crystal→ nematic or isotropic; ○, nematic→isotropic.

attributed to the wide variety of possible crystal structures. This has been shown to be the case for the *p*-alkoxybenzoic acids. An X-ray study [7] of these compounds revealed no similarities in crystal structure for the lower homologues; however, from *p*-*n*-heptyloxybenzoic acid onwards a similarity was found. These results are reflected in the crystal-to-mesophase transition temperatures [8], which change from a random to an even–odd alternation starting with the *p*-*n*-heptyloxy derivative. A similar effect was found in our first series of products which shows for the last four terms the characteristic alternation. 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 [9]. Nevertheless, from a comparison of

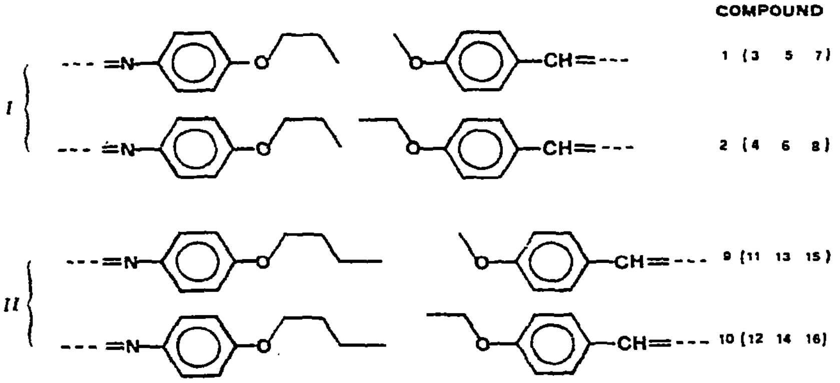

Fig. 3. Terminal situation of neighbouring molecules.

Figs. 1 and 2 one can note an increase in mesomorphic thermal stability of the compounds of the second series with respect to the corresponding compounds of the first. This can be qualitatively explained assuming the schematic molecular arrangements show in Fig. 3, where the terminal situation for compounds 1, 2, 9 and 10 is reported. The situations for the other compounds can be referred, in any case, to one of the same four molecular arrangements (numbers in parentheses in Fig. 3).

REFERENCES

1 D. Grasso, L. Abate, S. Fasone, C. Gandolfo and G. Siracusa, Thermochim. Acta, 43 (1981) 107. D. Grasso, C. Gandolfo, L. Abate, G. Buemi and S. Fasone, Thermochim. Acta, 46 (1981) 71.
2 E.M. Barral and M.J. Vogel, Thermochim. Acta, 1 (1970) 127.
3 C. Weigand and R. Gabler, Ber. Dtsch. Chem. Ges. B, 71 (1938) 2399.
4 Kei Murase, Bull. Chem. Soc. Jpn., 45 (1972) 1772.
5 J. Van Der Veen, W.H. De Jeu, A.H. Grobben and J. Boven, Mol. Cryst. Liq. Cryst., 17 (1972) 291.
6 J.P. Van Meter and B.H. Klanderman, Mol. Cryst. Liq. Cryst., 22 (1973) 271.
7 R.F. Bryen, J. Chem. Soc., (1960) 2517.
8 G.M. Bennett and B.J. Jones, J. Chem. Soc., (1939) 420.
9 G.W. Gray, Molecular Structure and Properties of Liquid Crystals, Academic Press, New York, 1962.