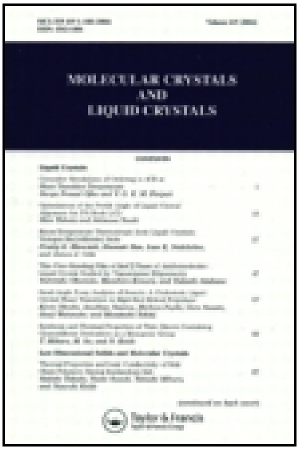

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Liquid Crystalline Behavior of Racemic Azobenzene Derivatives

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Liquid Crystalline Behavior of Racemic Azobenzene Derivatives

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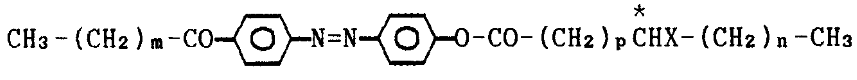
This paper deals with the synthesis of two series of racemic azobenzene derivatives of general formula:



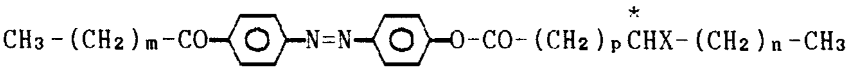
Using differential scanning calorimetry, optical microscopy and x-ray diffraction, the thermotropic liquid crystalline polymorphism of several methyl and chloro derivatives is studied: nematic, smectic A and monotropic smectic C mesophases are described.

INTRODUCTION

Over the few past years, we have been studying the synthesis and the thermotropic behavior of liquid crystals obtained from linear aliphatic derivatives of azobenzene.[1–2] These are generally either nematic or smectic in nature, with the molecules oriented perpendicular to the layers in the smectic phases.[3] In spite of a possible cis-trans isomerization of the azo-linkage, especially under the influence of ultraviolet light, all the mesophases encountered turned out to be surprisingly stable; repeated measurements of their polymorphic behavior invariably gave the same transition temperatures, even for samples stored over years in the dark.

Taking into account the growing interest in chiral mesogens leading to ferroelectric smectic materials, we decided to extend our studies to azobenzene derivatives with possibly chiral groups in the terminal chains. In this attempt we were encouraged by the known fact, first, that the introduction of branched aliphatic chains in smectogenic molecules generally favors the molecular tilting within the smectic layers (4) and, second, that the shortness of the azobenzene aromatic cores induces low viscosities, which is an important and useful property when looking for applications in the field of optical displays.

In this paper, we will be concerned with the chemical synthesis and the thermotropic liquid crystalline structural behavior of two series of azobenzene derivatives, apt to acquire optical activity and designated in the following by X-mnp:

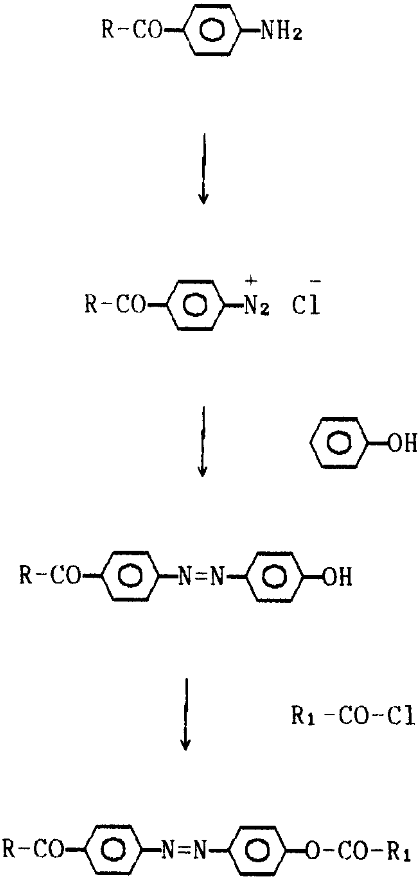


with $X = Cl$; $m = 0, 1, 2, 3, 4, 5$; $p = n = 0$

and $X = CH_3$; $m = 0, 1, 3, 4, 5$; $p = 0, 1$; $n = 2 - p$

SYNTHESIS

All the compounds considered in this work have been synthesized and purified by methods described previously,[1,2,5] following the reaction path:



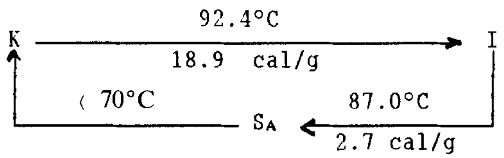
The amines with $m = 0{,}1$ were commerical products (Kodak, Aldrich), the others were prepared following the synthetic route proposed by Clifford *et al.*[5] The acid chlorides R_1—CO—Cl were prepared treating DL-2 and DL-3 methylvaleric acids (Aldrich) with $SOCl_2$.

THERMOTROPIC POLYMORPHISM

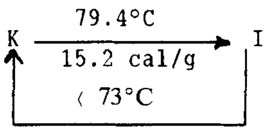
All the compounds synthesized were first investigated using differential scanning calorimetry (Perkin-Elmer VII, heating and cooling rates 5 and 0.3 K/min). It is of interest to note immediately that, among the chloro derivatives, only Cl-100 displayed an enantiotropic liquid crystalline phase, all the others passed directly from the crystalline to the liquid state. As for the smectic A to smectic C transitions of CH_3-311 and CH_3-511, detected upon cooling by optical microscopy or x-ray diffraction as stated below, the DSC thermograms did not show any exothermic peak, but just a small change of the baseline, indicative of a second order transition.

The mesophases were then studied by polarizing optical microscopy (Leitz-Orthoplan 2, Mettler FP82 hot stage). The nematic, smectic A and smectic C mesophases encountered were easily detected upon cooling from the melt and identified through their classical schlieren, focal conic, bâtonnet, and striated fan-shaped textures. Our DSC and microscopy observations are summarized in the following schemes:

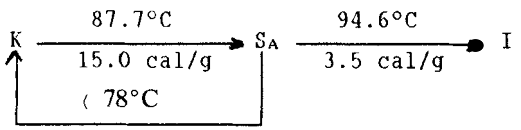
CH_3-011:



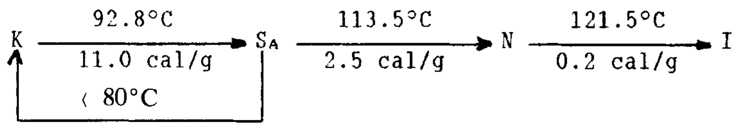
CH_3-020:



CH_3-120:



CH_3-111:



CH_3-311:

$$\begin{tikzcd}
K \arrow[r, "84.4^\circ\mathrm{C}", "11.0\ \mathrm{cal/g}"'] & S_A \arrow[r, "92.3^\circ\mathrm{C}", "0.6\ \mathrm{cal/g}"'] \arrow[d, dash] & N \arrow[r, "98.4^\circ\mathrm{C}", "0.3\ \mathrm{cal/g}"'] & I \\
S_C \arrow[u, "\langle\ 78^\circ\mathrm{C}"] & {} \arrow[l, "79.0^\circ\mathrm{C}"', "0\ \mathrm{cal/g}"] & &
\end{tikzcd}$$

CH_3-320:

$$\begin{tikzcd}
K \arrow[rr, "68.8^\circ\mathrm{C}", "19.6\ \mathrm{cal/g}"'] & & I \arrow[d, dash] \\
{} \arrow[u] & S_A \arrow[l, dash, "\langle\ 53^\circ\mathrm{C}"'] & {} \arrow[l, "60.4^\circ\mathrm{C}"', "2.0\ \mathrm{cal/g}"]
\end{tikzcd}$$

CH_3-411:

$$\begin{tikzcd}
K \arrow[r, "81^\circ\mathrm{C}", "12.1\ \mathrm{cal/g}"'] & S_A \arrow[r, "92.7^\circ\mathrm{C}", "0.6\ \mathrm{cal/g}"'] \arrow[d, dash] & N \arrow[r, "96.7^\circ\mathrm{C}", "0.4\ \mathrm{cal/g}"'] & I \\
S? \arrow[u] & {} \arrow[l, "81.1^\circ\mathrm{C}"', "0.4\ \mathrm{cal/g}"] & &
\end{tikzcd}$$

CH_3-420:

$$\begin{tikzcd}
K \arrow[rr, "68.7^\circ\mathrm{C}", "22.3\ \mathrm{cal/g}"'] & & I \arrow[d, dash] \\
{} \arrow[u] & S_A \arrow[l, dash, "\langle\ 53^\circ\mathrm{C}"'] & {} \arrow[l, "60.9^\circ\mathrm{C}"', "1.7\ \mathrm{cal/g}"]
\end{tikzcd}$$

CH_3-511:

$$\begin{tikzcd}
K \arrow[r, "83.9^\circ\mathrm{C}", "14.6\ \mathrm{cal/g}"'] & S_A \arrow[r, "96.0", "0.5\ \ \mathrm{cal/g}"'] \arrow[d, dash] & N \arrow[r, "99.8^\circ\mathrm{C}", "0.5\ \mathrm{cal/g}"'] & I \\
S_C \arrow[u, "\langle\ 65^\circ\mathrm{C}"] & {} \arrow[l, "82.7^\circ\mathrm{C}"', "0\ \mathrm{cal/g}"] & &
\end{tikzcd}$$

CH_3-520:

$$\begin{tikzcd}
K \arrow[r, "69.0^\circ\mathrm{C}", "16.2\ \mathrm{cal/g}"'] & S_A \arrow[r, "71.5^\circ\mathrm{C}", "2.2\ \mathrm{cal/g}"'] \arrow[d, dash] & I \\
{} \arrow[u] & {} \arrow[l, dash, "\langle\ 57^\circ\mathrm{C}"'] &
\end{tikzcd}$$

Cl-100:

$$\begin{tikzcd}
K \arrow[r, "140.6^\circ\mathrm{C}", "22.1\ \mathrm{cal/g}"'] & S_A \arrow[r, "148.4^\circ\mathrm{C}", "5.7\ \mathrm{cal/g}"'] \arrow[d, dash] & I \\
{} \arrow[u] & {} \arrow[l, dash, "\langle\ 139^\circ\mathrm{C}"'] &
\end{tikzcd}$$

STRUCTURAL BEHAVIOR

The mesophases detected were also studied by x-ray diffraction (Guinier focusing camera, bent quartz monochromator, copper Kα_1 radiation from a PW-1009 x-ray generator, home-made hot stage, patterns registered photographically). For the smectic phases, the patterns contained one, and sometimes two equidistant, sharp Bragg reflections in the small-angle region, indicative of a smectic layering, and one broad, generally very weak, scattering band in the wide-angle region, characteristic of the disordered arrangement of the molecules within the layers. The smectic periods, *d*, measured at temperature *T*, along with the molecular lengths, *L*, estimated by molecular modelling (Sybyl software from Tripos) are reported in the following table; they clearly indicate that the smectic structures are single-layered.

product	phase	L/A°	d/A°	T/°C
CH_3-011	A	22.0	23.1	86.5
CH_3-120	A	23.3	23.9	94.1
CH_3-111	A	23.5	23.5	112.0
CH_3-311	A	25.9	24.7	86.0
CH_3-311	C	25.9	—	—
CH_3-320	A	25.7	—	—
CH_3-411	A	26.3	25.2	82.0
CH_3-411	S?	26.3	—	—
CH_3-420	A	26.3	23.8	59.1
CH_3-511	A	28.5	26.8	91.5
CH_3-511	C	28.5	25.2	80.3
CH_3-520	A	27.9	26.2	71.2
Cl-100	A	20.8	21.4	140.0

It is important to note that the distinction between smectic A and smectic C phases using the above experimental data is far from being straightforward. First of all, the monotropic, and hence metastable, nature of the smectic C phase makes it extremely difficult to register photographically (exposure times of more than twelve hours) their diffraction patterns; thus, for CH_3-311 and CH_3-411 which appear upon cooling within a very narrow interval of temperature and which, in addition, exist only over very short periods of time, it was in fact impossible to register the corresponding diffraction patterns. Then, owing to the small difference between the periods of smectic A and C of CH_3-511, it is delicate to draw definite conclusions about the symmetry of the smectic phases from diffraction patterns registered at only a few temperatures. This is why, to ascertain the transition between smectic A and C phases of CH_3-511, we decided to employ a position-sensitive x-ray detector (CEA-LETI from INEL), which enables one to register upon cooling a whole set of x-ray patterns with an exposure time of only one or two minutes. Figure 1 shows that, in the range from 98 down to 83°C, the spacing of the smectic A phase remains perfectly constant at 26.7 A°, whereas in the range from 83 down to 65°C, where the sample starts to quickly crystallize, the spacing

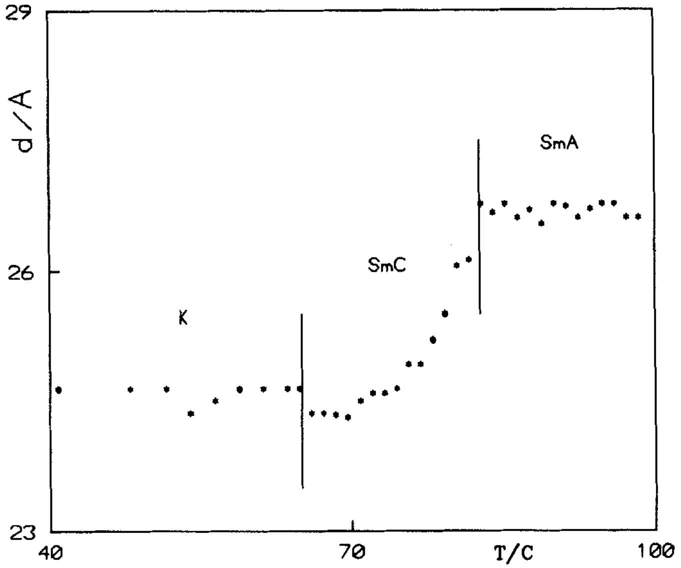


FIGURE 1 Smectic period of CH_3-511 as a function of decreasing temperature.

of the smectic C phase decreases from 26.7 to 24.4 A° with an almost vertical initial slope as expected for a second order transition and in full agreement with the DSC measurements.

CONCLUSION

The introduction of chiral moieties in the azobenzene derivatives does indeed favor the occurrence of smectic C phases. However, their frequency is rather poor; among the seventeen Cl-mnp and CH_3-mnp compounds considered, only three presented smectic C phases, that in addition were monotropic in nature. Close inspection of the variation of the melting temperature and of the smectic A/smectic C transition temperature with the number of methylene groups in the aliphatic chains suggests that compounds with longer terminal chains would probably lead to the formation of stable, enantiotropic smectic C phases. Interestingly, the presence of a chlorine atom in the α position of the chiral chain severely disfavors liquid crystallinity. Also, the presence of a methyl group in the β position of the chiral chain favors the formation of tilted smectic phases whereas in the α position, it only gives non-tilted smectic phases.

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