Synthesis and study of the mesomorphism of highly polarizable mesogens towards applications in non-linear optics

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Synthesis and study of the mesomorphism of highly polarizable mesogens towards applications in non-linear optics

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The synthesis of several 4-(4′-(4″-n-alkoxypiperidino)-trans-styryl)pyridine-N-oxides, a new liquid-crystalline series, is described. Its mesomorphic behaviour is studied, and it is shown that different members of the series exhibit partially bilayered smectic A phases; the degree of head-to-head association of the molecules, in the smectic A phase, is found to decrease when the temperature or the length of the aliphatic chain increases. This new type of smectogen should possess interesting non-linear optical properties.

1. Introduction

It has been demonstrated that organic compounds can yield efficient materials for non-linear optical applications [1–4]. Compared to their inorganic counterparts, organic molecules have the advantages of higher polarizabilities and of less sensitivity to damage by laser irradiation. In most cases, optical studies have been performed on solid condensed phases: single crystals or powders. Only a few publications have been devoted to the use of liquid crystals [5–8]. The electric field associated with a photon $E \sim E_0 \cos \omega t$ generated an induced polarization of an isolated molecular unit which can be expressed as

$$\mu = \alpha E + \beta E^2 + \gamma E^3 + \dots. \tag{1}$$

The second order hyperpolarizability parameter is the term responsible for the generation of the second harmonic. On a macroscopic scale, the summation of the individual electric dipoles leads to an induced polarization of the material [1, 3];

$$P = X_1 E + X_2 E^2 + X_3 E^3 + \dots. \tag{2}$$

Both the molecular unit and the molecular material must be non-centrosymmetric in order to have non-zero second order coefficients. Consequently, an electric field is applied to the nematic or smectic mesophase so as to orient partially the molecules and to favour the head-to-tail arrangement over the head-to-head one.

A mesogen which can efficiently lead to second harmonic generation must have the following characteristics. It must be highly polarizable. This feature may be inferred from the presence of an intramolecular charge-transfer band in the optical absorption spectrum [9, 10]. It must also have a high permanent dipole moment so

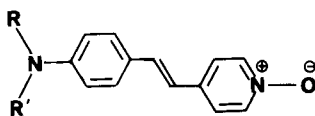† Groupe de Recherches Interdisciplinaires sur les Matériaux Moléculaires.

Figure 1.   Molecular structure of the alkylamino-azastilbene-*N*-oxide derivatives.

as to permit orientation of the liquid crystal under electric fields. For these reasons, we first decided to consider alkylamino-azastilbene-*N*-oxide derivatives (cf. figure 1). The permanent dipole of this type of molecule is $6.9\,D$ ($1\,D = 3.338 \times 10^{-30}\,C\,m$); it possesses an intramolecular charge-transfer band at $3.1\,eV$ (400 nm) with a high absorption coefficient. Indeed, determination of non-linear properties in solution indicates an exceptionally high value of β (500×10^{-30} e.s.u. where 1 e.s.u. $= 3.712 \times 10^{-21}\,C^3\,m^3\,J^{-2}$) [11] compared to usual nitroaniline derivatives ($\beta \sim 35 \times 10^{-30}$ e.s.u.). Although some of the pyridine-*N*-oxide derivatives have been previously found to produce liquid-crystalline phases [12], products illustrated in figure 1 with $R = CH_3$ and $R' = C_8H_{17}$ do not apparently exhibit liquid-crystalline phases, probably due to the presence of the lateral $R = CH_3$ group, protruding with respect to the molecule, and thus spoiling the linearity of the molecule. To preserve this linearity, we decided finally to consider mesogens in which the nitrogen atom is included in a symmetrical cyclohexane ring. In this paper, the synthesis of four new mesogens based on the azastilbene *N*-oxide sub-unit and the structure of the corresponding mesophases are described.

2.   Synthesis

The chemical pathway shown in figure 2 was used to synthesize the various mesogens. 4-fluorobenzaldehyde was reacted with 4-hydroxypiperidine under standard experimental conditions [13] to yield **6**. The condensation of 4-(4'-hydroxypiperidino)-benzaldehyde **6** with 4-picoline *N*-oxide was achieved using procedures similar to those described in the literature [14–17]. In the present case, a quaternary ammonium hydroxyde (Triton B), instead of potassium hydroxide or sodium methoxide, was used as the base. The various mesogens were obtained by reacting the corresponding
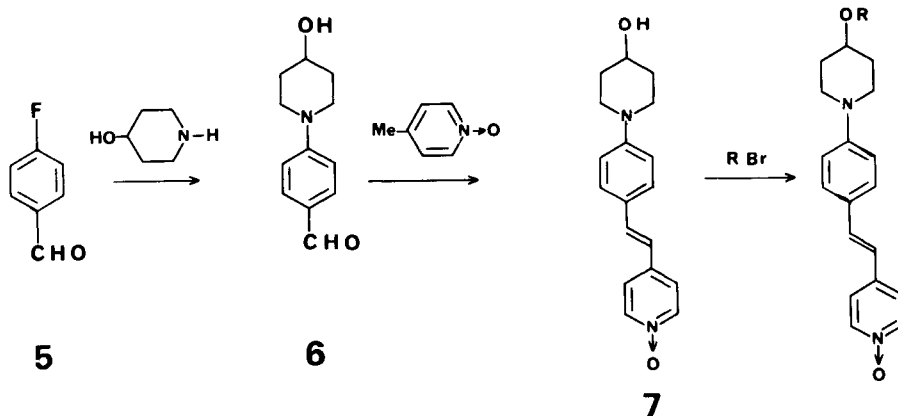

Figure 2.   Chemical pathway used to synthesize mesogens. 1, $R = C_6$; 2, $R = C_8$;
3, $R = C_{12}$; $R = C_{18}$.

bromide with compound 7 in dimethylsulphoxide in the presence of powdered potass-
ium hydroxide. The reaction probably occurs at the surface of the solid potassium
hydroxide [18]. This method gives a mixture of the cis and trans isomers which must
subsequently be separated by chromatography.

3. Mesomorphic behaviour

The transition temperatures were determined from differential scanning calori-
metry (D.S.C.) and from optical microscopy using polarized light. The D.S.C. exper-
iments were performed on a D.S.C. II Perkin–Elmer apparatus, with heating and
cooling rates of 2·5°C/min. The optical experiments were performed using an Ortho-
plan Leitz microscope equipped with a FP52 Mettler hot stage.

All of the samples are yellow in their crystalline state, and become red upon
entering the mesomorphic phase, at a temperature between 120 and 130°C, depending
upon the length of the aliphatic chain. The mesomorphic phase has been identified as
smectic A, since classical 'bâtonnets' [19] appear and grow when cooling into this phase
from the isotropic phase, and since homeotropic areas are also evident within the
domain of stability of the mesophase.

Table 1. Transition temperatures as determined by differential scanning calorimetry (D.S.C.)
and optical microscopy (O.M.). Numbers in brackets are the latent heat of transition in
J/g.

n	$T/°C$ (D.S.C.)	$T/°C$ (O.M.)	
	$K \rightarrow S_A$	$K \rightarrow S_A$	$S_A \rightarrow I$
6	126	129	168
8	128 (80·3)	129	179–184
12	121 (81·2)	122	172–183
18	117 (84·5)	122	170

All the experimental data are gathered in table 1. It should be noted that the
members of the series with $n = 8$ and $n = 12$ become isotropic over a relatively large
temperature range (5 to 10°C), with some degradation occurring simultaneously. The
width of the transition temperature intervals results from the difficulty of removing
traces of water from the mesogens, which are highly hygroscopic. The clearing
temperatures are completely reversible, whereas a strong supercooling of about 40°C
is observed for the smectic A to crystalline transition.

4. X-ray diffraction

X-ray diffraction experiments were performed using a Guinier type camera,
equipped with a bent quartz monochromator (using K_{α_1} radiation) and an electric
oven, the temperature of which was regulated to within 0·1°C. X-ray patterns of the
smectic A phase for all members of the series show a sharp Bragg reflection in the low
angle region and a diffuse band in the wide angle region corresponding to about 4·4 Å.
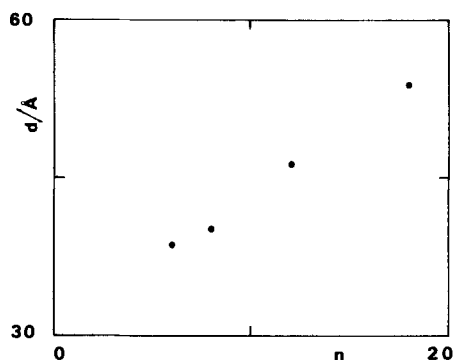The sharp reflection results from stacking of the smectic layers and the diffuse band

Figure 3.   Layer spacing, d, in the smectic A phase as a function of the length of the aliphatic chain at 130°C.

Table 2.   Values of the structural parameters at $T = 130$°C for the different members of the series: d is the layer spacing in the smectic A phase as determined from X-ray diffraction experiments, l is the length of the molecule measured from CPK atomic models, and τ is the degree of head-to-head association of the molecules.

n	$d\,(S_A)/\text{\AA}$	$l/\text{\AA}$	d/l	τ
6	38·6	24·7	1·56	0·72
8	40·2	27·2	1·48	0·65
12	46·3	32·1	1·44	0·61
18	53·8	39·6	1·35	0·53

from the liquid-like arrangement of the molecules within the layers, as is typical of smectic A phases.

As shown in table 2, the value of the layer spacing, d, for each compound is intermediate between one and two molecular lengths (as obtained from CPK models with the aliphatic chains in their most extended conformation). Like the liquid-crystalline N-oxide compounds previously studied [20], all the members of this new series exhibit the smectic A phase with partial bilayering [21, 22]. This is confirmed by the linear variation of d as a function of the number, n, of carbon atoms in the aliphatic chain (cf. figure 3); the increase in d per methylene group is 1·35 Å which is larger than the 1·27 Å expected for a paraffinic chain in its most extended conformation.

Figure 4 shows the variation of the layer spacing as a function of temperature in the crystalline and in the smectic A phases for the $n = 8$ member of the series. The increase in d with decreasing temperature in the smectic phase must be related to the degree of association, τ, of the molecules; indeed, it is now well known that this type of unsymmetric molecule can associate head-to-head in pairs through their dipolar end groups [20, 21]. From [21], d and τ are related by

$$d/l = 2/(2 - \tau),$$

where l is the molecular length. The corresponding variation of τ as a function of temperature is shown in figure 5. As the temperature increases, the degree of head-to-head association, τ, decreases by about 20 per cent. This corresponds to an increase of the average molecular area of the paraffinic tails, which therefore leads to a reduction of the stretching of the disordered aliphatic chains and of the elastic
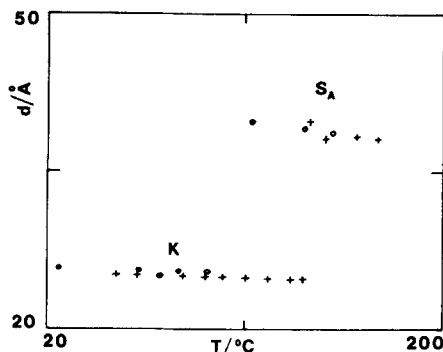
Figure 4. Layer spacing, *d*, of the *n* = 8 member of the series as a function of temperature (+, increasing temperature; O, decreasing temperature).
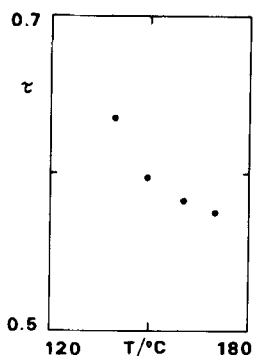

Figure 5.   Degree of association, τ, as a function of temperature for the *n* = 8 member of the series.

contribution to the entropy of the chains with respect to the overall energy. Clearly, the disordering of the aliphatic chains hinders the head-to-head association of the polar molecules.

An analogous effect can be found in connection with the length of the aliphatic chain. As *n* increases from 6 to 18, τ decreases from 0·72 to 0·53 (see table 2). This can be understood from the fact that as *n* increases, the paraffinic elastic density increases, and therefore the association of the molecules becomes less favourable [21].

5. Conclusion

In this paper, we have shown that 4-(4′-(4″-*n*-alkoxypiperidino)-trans-styryl)-pyridine-*N*-oxides are able to produce smectic A liquid-crystalline phases, partially bilayered as usual for unsymmetric highly polar mesogens. The degree of head-to-head association of the molecules, enhancing the bilayer smectic character, was shown to decrease when the temperature or the length of the aliphatic chain increases, due to the elasticity of the disordered aliphatic chains.

This new family of smectogens should possess interesting non-linear optical properties due to the high electric dipole moment carried by the molecules, more especially as the degree of association, and consequently the local ferro-electric arrangement of the molecules can apparently be easily controlled by varying the temperature and the length of the aliphatic chain.

6. Experimental section

4-(4′-hydroxypiperidino) benzaldehyde 2·5 g (20 mmol) of 4-fluorobenzaldehyde, 3 g (30 mmol) of 4-hydroxypiperidine and 3·5 g of anhydrous potassium carbonate were stirred and heated at 90°C for 48 hours in 3 ml of DMSO. The reaction mixture is then diluted with 50 ml of water. The precipitate was recrystallized from a chloroform/ cyclohexane mixture.

Yield: 75 per cent. m.p. = 118·8°C.

Analysis: calculated: C = 70·22; H = 7·37; N = 6·82
                  Found: C = 70·37; H = 7·57; N = 6·84.

^{1}H N.M.R. (CDCl$_3$, TMS) 1·75 (m, 4H, CH$_2$), 2·30 (br, 1H, OH),
          3·15 (m, 2H, NCH$_2$), 3·83 (m, 3H, OCH + NCH$_2$),
          6·88 (d, J9·0 Hz, 2H, Ar), 7·72 (d, J9·0 Hz, 2H, Ar),
          9·75 (s, 1H, CHO).

U.V. (ethanol): 343 nm (log ε = 4·43).

4-(4′-4″-hydroxypiperidino)-trans-styryl)pyridine-N-oxide 10 g (50 mmol) of 4-(4′-hydroxypiperidino)benzaldehyde, 6·5 g (60 mmol) of 4-picoline-*N*-oxide and 21 g (50 mmol) of a 40 per cent wt solution of benzyl trimethyl ammonium hydroxide (Triton B) in methanol were refluxed in 60 ml of dry methanol. After 2 hours, the solvent was evaporated and the residue treated with a mixture of chloroform and ice. The crude product was recrystallized in two litres of a mixture of chloroform and iso-propanol (1 : 1), and dried by azeotropic distillation of toluene.

Yield: 70 per cent, decomposes near 220°C.

Analysis: calculated: C = 72·95; H = 6·80; N = 9.45.
                  Found: C = 72·88; H = 6·90; N = 9·42.

^{1}H N.M.R. (CDCl$_3$ + CD$_3$OD (1 : 1), TMS) 1·85 (m, 4H, CH$_2$),
          2·98 (m, 2H, NCH$_2$), 3·73 (m, 3H, NCH$_2$ + CH),
          4·56 (br, OH), 6·87 (d, J16·5 Hz, 1H, PhCH),
          6·95 (d, J9·3 Hz, 2H, Ar), 7·28 (d, J16·2 Hz, 1H, PyrCH),
          7·47 (d, J9·3 Hz, 2H, Ar), 7·53 (d, J7·2 Hz, 2H, β Pyr),
          8·18 (d, J7·2 Hz, 2H, α·Pyr)

Table 3.   Yields and elemental analyses for the 4-(4′-(4″-*n*-alkyloxypiperidino)-trans-styryl)-pyridine-*N*-oxides.

R	Yield (per cent)	Analysis	
		Calculated	Found
n-C$_6$H$_{13}$ (1)	13	C 75·75 H 8·46 N 7·36	C 72·16 H 8·39 N 6·66
n-C$_8$H$_{17}$ (2)	12	C 76·43 H 8·88 N 6·86 H$_2$O 0·00	C 76·15 H 9·05 N 6·86 H$_2$O 0·47
n-C$_{12}$H$_{25}$ (3)	18	C 77·54 H 9·54 N 6·03	C 76·48 H 9·65 N 5·82
n-C$_{18}$H$_{37}$ (4)	15	C 78·78 H 10·28 N 5·10	C 76·50 H 10·31 N 4·75

U.V.-Vis. (Ethanol + chloroform, 9:1): 391 nm ($\log \varepsilon = 4\cdot31$)

4-(4'-(4"-n-alkoxypiperidino)-trans-styryl)pyridine-N-oxide 1·45 g (4·9 mmol) of 4-(4'-(4"-hydroxypiperidino)-trans-styryl)pyridine-N-oxide and 15 g of finely ground potassium hydroxide were stirred together in 10 ml of dry DMSO. The corresponding alkyl halide (10 mmol) was then added and the mixture further stirred for 24 hours at room temperature. 250 ml of water were added and the aqueous layer extracted twice with 100 ml of benzene; the oily residue obtained by evaporation of the organic layers was filtered on silica (eluent: acetone/methanol). The trans-isomers of the title compound were separated by HPLC (eluent: dichloromethane, ether, methanol (3:6:1)). The yellow solids obtained were dried by evaporation of eluent and azeotropic distillation in toluene. The yields and elemental analysis are given in table 3.

^{1}H N.M.R. (CDCl$_3$, TMS) of the C$_8$ derivative:

0·88 (t, J6·5 Hz, 3H, CH$_3$), 1·3 (br, 10H, CH$_2$),

1·57 (m, 2H, CH$_2$), 1·72 (m, 2H, CH$_2$),

2·0 (m, >2H, CH$_2$ + εH$_2$O), 3·03 (m, 2H, NCH$_2$),

3·47 (t + m, J6·6 Hz, 3H, NCH$_2$ + OCH), 3·60 (m, 2H, NCH$_2$).

6·78 (d, J16·3 Hz, 1H, PhCH), 6·91 (d, J8·9 Hz, 2H, Ar),

7·09 (d, J16·2 Hz, 1H, PyrCH), 7·31 (d, J7·2 Hz, 2H, β Pyr),

7·40 (d, J8·8 Hz, 2H, Ar), 8·12 (d, J7·1 Hz, 2H, α Pyr).

U.V.-Vis (methanol): 392 nm ($\log \varepsilon = 4\cdot45$) for the C$_{18}$ derivative.

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