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Structure of the Smectic A Mesophase of the N-Oxides of Certain 4-(4′-n-Alkoxyphenyl)Pyridines

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Structure of the Smectic A Mesophase of the *N*-Oxides of Certain 4−(4′−*n*−Alkoxyphenyl)pyridines

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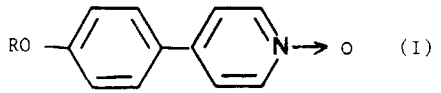
The structure of the smectic A mesophase formed by the *N*-oxides of two 4-(4′-*n*-alkoxyphenyl)pyridines has been studied by X-ray diffraction. The thickness of the layers was found to be intermediate between one and two molecular lengths. This result has been interpreted within the framework of a model proposed recently to describe the behavior of partially bilayered smectic A phases of highly polar and dissymmetric mesogens and the degree of head-to-head association of the molecules found to be larger for the *N*-oxides than that determined for cyanobiphenyls.

INTRODUCTION

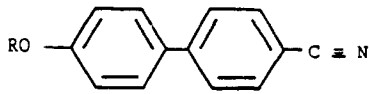
The structural and physical properties of dissymmetric and highly polar mesogens are now well known to be quite unusual, both for the smectic A and for the nematic mesophase. The smectic state is characterized by the existence of layers the thickness of which ranges from one to two molecular lengths[1–5] and the nematic phase occurs

not only at temperatures above the stability domain of the smectic phase, but also at temperatures below it (reentrant nematic[2]). For the smectic A phase, a model has been proposed recently[6] in which the smectic layers are described in terms of a mixture of single molecules and of pairs of molecules associated head-to-head. Until now these properties have been observed only when the dipolar end of the molecule is a cyano[1,3,4] or a nitro[4,5] group.

In this letter, we report the results of an X-ray investigation of new dissymmetric and very polar mesogens formed by the *N*-oxides of 4-(4′-*n*-alkoxyphenyl)pyridines (I).



(I)



(II)

The synthesis and properties of these liquid crystals have been published elsewhere.[7] Their special properties are due to the presence at the end of the molecules of a dipole moment (4.61 Debye), stronger than that of the cyano end group (4.33 Debye) of the 4′-*n*-alkoxy-4-cyanobiphenyls (II).[1]

RESULTS

X-Ray experiments were performed with the aid of a Guinier camera equipped with a bent quartz monochromator, using the CuK_{α_1} radiation. Two homologues ($R = C_7H_{15}$ and $R = C_{12}H_{25}$) of series (I) have been investigated. The following transition temperatures have been reported for these compounds:

$$R = C_7H_5 \quad I \xrightarrow{72°C} S_A \xrightarrow{\sim 50°C} K$$

$$R = C_{12}H_{25} \quad I \xrightarrow{110.5°C} S_A \xrightarrow{\sim 65°C} K$$

Figure 1 illustrates the variation of the layer spacing, *d*, of the smectic A phase as a function of temperature for the two compounds. In both cases, *d* decreases slightly as the temperature increases: from 29.8 to 29.4 Å for C_7, and from 36.8 to 35.3 Å for C_{12}.

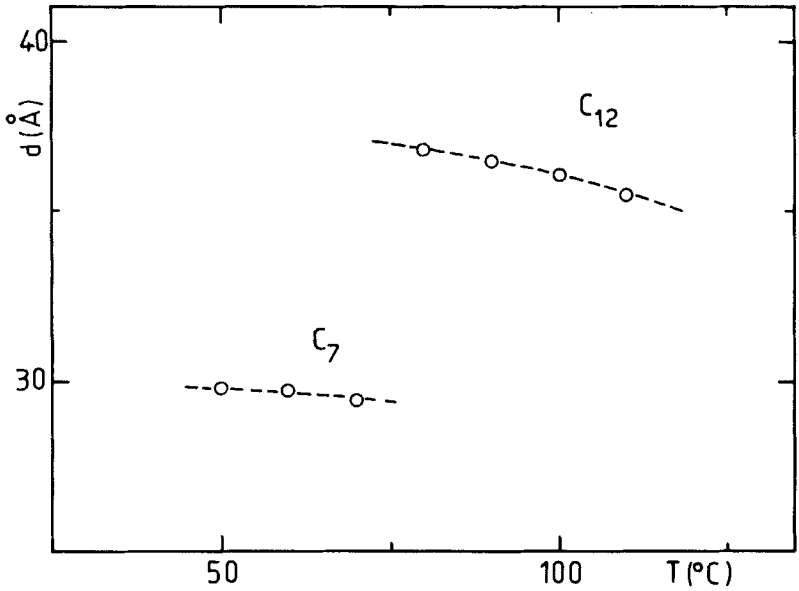


FIGURE 1 Layer spacing, d, in the smectic A phase as a function of temperature.

As in the case of the cyanobiphenyls, the layer spacing, d, is intermediate between one and two molecular lengths (the molecular length, l, having values of ~21 Å for C_7 and ~27 Å for C_{12}). In Table I, are reported the values of the ratio d/l as a function of temperature, and the values of τ, the degree of head-to-head association of the molecules, calculated using the relation: $d/l = 2/(2 - \tau)$,[6] for the compounds of series (I).

TABLE I

Layer spacing, d, ratio d/l (layer spacing/molecular length) and degree of head-to-head association, τ, of the molecules in the smectic A phase as a function of temperature for the two compounds of series (I)

R	T(°C)	d(Å)	d/l	τ
C_7H_{15}	70	29.4	1.40	0.57
	60	29.8	1.42	0.59
	50	29.8	1.42	0.59
$C_{12}H_{25}$	100	35.4	1.31	0.48
	100	36.1	1.34	0.50
	90	36.4	1.35	0.52
	80	36.8	1.36	0.53

TABLE II

Layer spacing, d, ratio d/l (layer spacing/molecular length) and degree of head-to-head association, τ, of the molecules in the smectic A phase for the compounds of series (II). Values in brackets are early values reported by Leadbetter and his co-workers[8]

R	T(°C)	d(Å)	$d/_l$	τ
C_8H_{17}	62	31.3(32)	1.35	0.52
$C_{10}H_{21}$	75	34.7(35.4)	1.34	0.51
$C_{12}H_{25}$	75	37.9(41.6)	1.34	0.51

In Table II, are reported the values of the same structural parameters for the compounds of series (II).

CONCLUSION

From these results, it is clear that the structure of the smectic A phase of the *N*-oxides is closely similar to that of the cyanobiphenyls. However, the degree of head-to-head association of the molecules, although of the same order of magnitude in the two series, is found to be slightly larger for the *N*-oxides. This illustrates the powerful influence of the strong terminal dipole moment.

It is also noteworthy that the degree of head-to-head association is larger for the C_7 (0.58 ± 0.01) than for the C_{12} derivative of the *N*-oxides (0.51 ± 0.02). This can be attributed to the disordered conformation of the aliphatic chains. Indeed, as mentioned elsewhere,[6] the lateral space needed for an aliphatic chain to adopt a disordered conformation increases with the molecular weight, and, as a consequence, the head-to-head association of the molecules must decrease, in order to enlarge the lateral extension of the layers.

Finally, it is of interest to point out that the X-ray diffraction pattern of the C_7 *N*-oxide exhibits two orders of diffraction corresponding to the layer spacing, whereas the C_{12} *N*-oxide shows only one. This is presumably due to the relative thicknesses of the aromatic and aliphatic sublayers which are roughly the same (~18 Å) for the

† The average thickness of the aromatic sublayer, d_a, can be easily evaluated from the length of the aromatic core of the molecules ($l_a \sim 13$ Å according to CPK molecular models) and from the degree of head-to-head association, τ, of the molecules: $d_a = l_a x 2/(2 - \tau)$. The average thickness of the aliphatic sublayers, d_p, is of course $d_p = d - d_a$.

C_{12} *N*-oxide, but are different for the C_7 compound ($l_{aromatic} \sim 19$ Å and $l_{aliphatic} \sim 10$ Å).† The interfaces between the aromatic and aliphatic sublayers are rather diffuse, due to the presence in the layers of monomers and dimers of different length, and also to the Debye–Waller thermal effect. When of the same order of magnitude, as for the C_7 and C_{12} *N*-oxides, the thickness of the interfaces produces the same attenuation of the intensity of the higher orders of diffraction. The absence of the second order of diffraction for the C_{12} compound is therefore due only to the structure factor of the system.

References

1. G. W. Gray and J. F. Lydon, *Nature* **252**, 221 (1974); J. E. Lydon and C. J. Coakley, *J. Phys.* **36C1**, 45 (1975).
2. P. E. Cladis, *Phys. Rev. Lett.*, **35**, 48 (1975).
3. P. Seurin, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.* **71**, 37 (1981).
4. F. Hardouin, A. M. Levelut, M. F. Achard and G. Sigaud, *J. de Chim. Phys.* **80**, 53 (1983).
5. A. C. Griffin, R. F. Fisher and S. J. Havens, *J. Am. Chem. Soc.* **100**, 6329 (1978).
6. D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.* **91**, 341 (1983); D. Guillon and A. Skoulios, *J. Phys.* **45**, 607 (1984).
7. D. J. Byron, D. Lacey and R. C. Wilson, *Mol. Cryst. Liq. Cryst.* **76**, 253 (1981).
8. A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray and A. Mosley, *J. Phys.* **40**, 375 (1979).