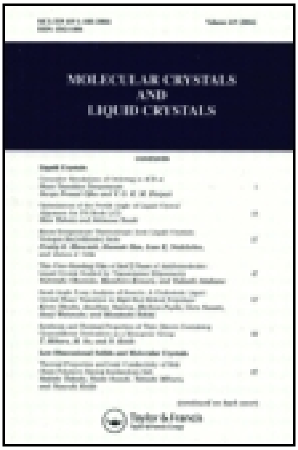


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

On Some New Series of Biforked Mesogens

C. Destrade [a], Nguyen Huu Tinh [a], A. Roubineau [b] & A. M. Levelut [c]

[a] Centre de Recherche Paul Pascal, Domaine Universitaire, 33405, Talence Cedex, France

[b] Ecole Nationals Supérieure de Chimie et de Physique de Bordeaux, 351, cours de la Libération, 33405, Talence Cedex, France

[c] Laboratoire de Physique des Solides, Bătiment 510, 91405, Orsay Cedex, France

Version of record first published: 19 Dec 2006.

To cite this article: C. Destrade , Nguyen Huu Tinh , A. Roubineau & A. M. Levelut (1988): On Some New Series of Biforked Mesogens, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 159:1, 163-171

To link to this article: http://dx.doi.org/10.1080/00268948808075269

Mol. Cryst. Liq. Cryst., 1988, Vol. 159, pp. 163–171
Photocopying permitted by license only

Printed in the United States of America

On Some New Series of Biforked Mesogens

C. DESTRADE and NGUYEN HUU TINH

Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence Cedex, France

A. ROUBINEAU

Ecole Nationale Supérieure de Chimie et de Physique de Bordeaux, 351, cours de la Libération, 33405 Talence Cedex, France

and

A. M. LEVELUT

Laboratoire de Physique des Solides, Bâtiment 510, 91405 Orsay Cedex, France

(*Received July 3, 1987*)

Two series of biforked mesogens derived from 3,4- or 3,5-dialkoxybenzoic acids are described. The 3,5-derivatives exhibit only one hexagonal columnar mesophase, but the 3,4-derivatives display an interesting polymorphism such that phases with both columnar and lamellar mesomorphic order exist for the same sample. The relationship between this behaviour and the number and position of the substituents is discussed.

Keywords: biforked mesogens, hexagonal columnar phase, columnar/lamellar polymorphism

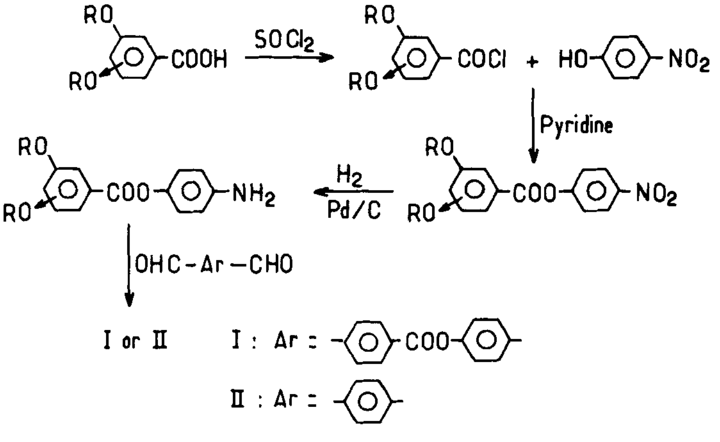
INTRODUCTION

Besides rod-like and disc-like mesogenic molecules, several new kinds of molecular design have been shown to lead to thermotropic mesophases, e.g., cone-shaped,[1] macrocyclic,[2] forked[3] and biforked[4] mesogens, and also phasmidic molecules.[5] Considering the three last examples, the purpose of the research to which the above references relate was to obtain thermotropic nematic phases with biaxial properties: the molecules studied consist of a classical nematogenic rod-like part with something like a half-disk part at both extremities. Biaxial nematic behaviour has in fact been demonstrated in a pure thermotropic material corresponding to this molecular design,[6] and furthermore, a direct uniaxial nematic to biaxial nematic has been demonstrated (Nu–Nb).[6] Moreover the so-called *biforked mesogens* exhibit a rich variety of mesophases and mesomorphic sequences including lamellar, columnar phases, ribbon phases and nematic phases.[4]

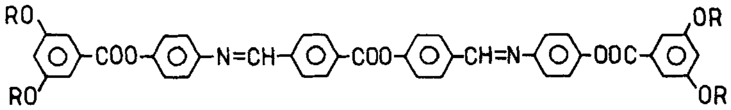
An extensive exploration of such kinds of material is now in progress, and we report here on two homologous series of biforked mesogens in which we have checked the role of the length of the rod-like part and of the *para*- or *meta*-substituents on the terminal benzene rings on the mesomorphic behavior.

SYNTHESIS

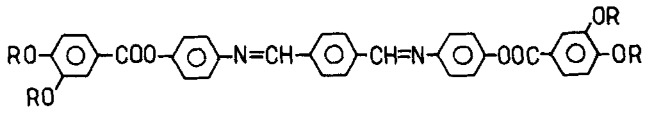
The two series I and II of biforked mesogens were prepared following the same general scheme starting from 3,4- or 3,5-dialkoxybenzoic acids.



I



II



RESULTS

Phase transitions were studied by polarizing microscopy in conjunction with a Mettler PF5 unit, and by differential scanning calorimetry (Perkin Elmer); X-ray diffraction was used to determine the symmetry properties of the mesophases. The structural information was derived mainly from diffraction patterns obtained from powder samples with a classical Guinier camera. In some cases, when orientation of the mesophases was possible, X-ray patterns of magnetically aligned samples were obtained.

1. Series I

TABLE I

Transition temperature of the compounds I

n	K	ϕ_h	I	a (Å)
7	· 110°	[· 104°]	·	
9	· 96°	· 112°	·	43.8
10	· 76°	· 116°	·	46.1
12	· 68°	· 116°	·	49.6
	(8.76)	(0.65)		

Enthalpies (Kcal·mole^{-1}) are given in brackets
ϕ_h = hexagonal columnar phase; K = crystal; I = isotropic
a = hexagonal lattice parameter

Within the series, only one type of mesophase was detected by optical observation. The textures are fan shaped (Figure 1), with developable domains in every way similar to those of conventional columnar mesophase,[7] especially those of hexagonal columnar mesophases. The K–M and M–I enthalpies are also comparable.

The powder pattern registered within the mesomorphic temperature range contains a few sharp Bragg reflections in the small-angle region and a diffuse ring at 4.6 Å. This ring is characteristic of the melted state of the paraffinic moieties of the molecules. The reciprocal spacings of the sharp reflections are typical of a two dimensional hexagonal lattice.

Despite the unusual length of the central rigid part (six benzene rings), the transition temperatures are surprisingly low, a fact evidently connected with the *meta*-disposition of all the alkoxy substituents.

We have also synthesized homologous compounds with only five benzene rings: the mesophases are only monotropic at around room temperature. The phases are probably ϕ_h columnar phase and S_C lamellar phase in the case of short chains.

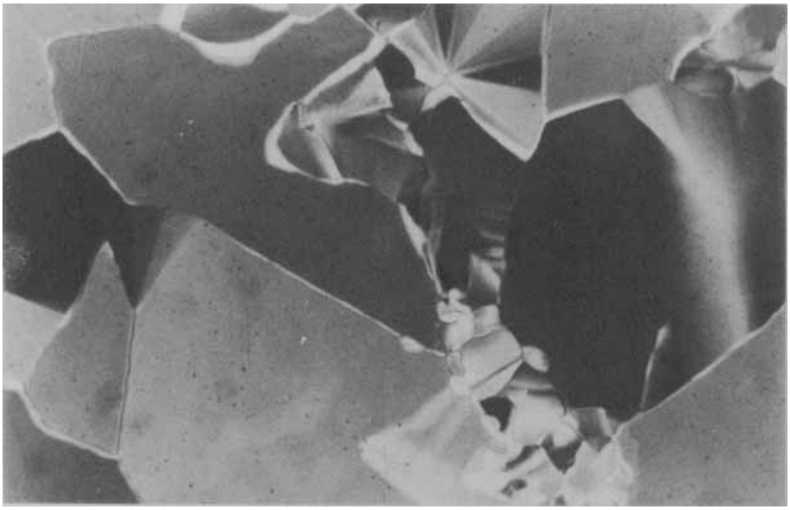


FIGURE 1 Optical texture of the ϕ_h phase of compound I (C_9H_{19}) at 100°C.

2. Series II.

We have carried out a more extensive study of series II which provides a rather rich polymorphism.

TABLE II

n	K	S_C	ϕ_{ob}	ϕ_h	N	I
6	· 160 (6.7)	· 200 (1.48)	—	—	· 240 (0.25)	·
7	· 138	· 199.5	—	—	· 223.5	·
8	· 137 (15.5)	· 198.5 (1.55)	—	—	· 206.5 (0.16)	·
9	· 130	· 191	—	—	—	·
10	· 125 (13.9)[a]	· 185 (1.37)	—	—	—	·
11	· 129 (15.4)	· 154 (0.10)	· 170 (0.41)	· 187 (1.23)	—	·
12	· 127.5 (17.2)	· 128.5 (0.20)	· 161 (0.30)	· 186 (1.32)	—	·
14	· 123 (21.2)	—	—	· 176 (1.42)	—	·

K = crystal

[a] K_1 to K_2 transition at 110°C (4.4)

Enthalpies ($\mathrm{Kcal \cdot mole^{-1}}$) are given in brackets

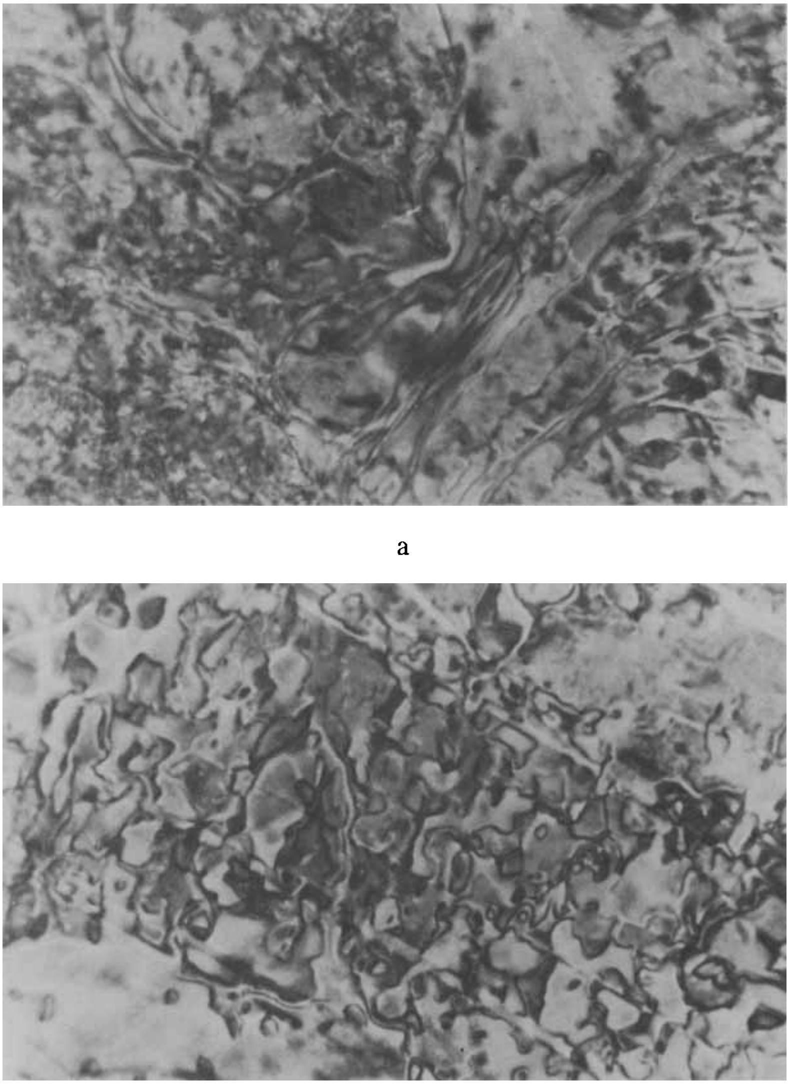
ϕ_{ob} = oblique lamello-columnar phase (see text)

ϕ_h = hexagonal columnar phase

N = nematic

I = isotropic

Short chain derivatives (C_6 to C_8) exhibit two mesophases unambiguously identified by their optical texture as a lamellar smectic C phase (Figure 2a) and a nematic phase (Figure 2b). The S_C phases show a particularly interesting behaviour—strong thermal fluctuations which are probably connected with an unusually low viscosity



a

b

FIGURE 2 Optical texture of compound II (C_8H_{17}): a) S_C phase at 187°C. b) N phase at 200°C.

and a strong birefringence. The X-ray patterns indicate that the tilt angle reaches ≃50° in this phase.

Concerning the nematic phase, careful optical observations[8] show the reversible appearance of zig-zag lines 1°C below the clearing point. It is noted that such zig-zag lines are characteristic of a biaxial nematic provided that these lines are not effectively linked to the glass surface. If we presume that the phase is a Nbx phase, we are not in fact able to claim that the lines do not lie at the interface.

Those derivatives with C_9 and C_{10} substituents show only a S_C phase over a large temperature range.

By way of contrast, derivatives with C_{11} and C_{12} chains exhibit an interesting polymorphism with a lamellar phase (S_C) at lower temperatures and a columnar phase (ϕ_h) (Figure 3a) at higher temperatures. The passage between the lamellar and columnar phases is realised in both cases *via* an intermediate phase (Figure 3b), with an oblique 2D lattice; this phase we call a *lamello-columnar* mesophase. This phase has the structure of a ribbon phase like ϕ_{ob},[4] the lattice parameters being: $a = 33.4$ Å, $c = 59.5$ Å, $\beta = 145°$ (C_{11} derivative). The thickness of a ribbon ($c.\sin\beta$) is equal to the layer thickness of the smectic phase at lower temperatures. The layer thickness of the S_C phase is 34.1 Å, while the lattice constant of the hexagonal columnar phase is $a = 46.9$ Å, a value very similar to that obtained with the corresponding phasmidic compound,[5] for which $a = 46$ Å for the C_{12} derivative.

Finally, the longest chain homologues, C_{13} and C_{14}, give evidence of only one mesomorphic phase (ϕ_h). The optical textures of this mesophase are in every way similar to those of the compounds of series I. Furthermore, the X-ray patterns demonstrate an hexagonal 2D lattice with $a = 49.7$ Å (C_{14} derivative). The structure of this phase is extensively discussed in References 5 and 10.

More and more polysubstituted mesogenic materials have now been achieved (polycatenar mesogens) with six chains (phasmids), four chains (biforked mesogens) and several other combinations (Figure 4).[11] Looking at the number and position (4-*ortho* or 3-*meta*) of the alkoxy substituents, a clear relationship between molecular design and mesomorphic properties can be emphasised: the columnar behaviour is clearly connected with the *meta*-arrangement, whereas the *ortho*-disposition favours (by evidence) lamellar phases. Therefore it is now easy to understand why type **3** molecules (Figure 4) can give both lamellar and columnar mesophases, while type **2** molecules give only columnar mesophases.

FIGURE 3 Optical texture of compound II ($C_{11}H_{23}$): a) ϕ_h phase at 184°C. b) ϕ_{ob} → ϕ_h phase at 170°C.

Compound design	Number of substituents in the 6-position	Number of substituents in the 3-position	Lamellar phases	Columnar Phases
1	2	4	no	yes
2				yes
	0	4	no	yes
3	2	2	yes	no
4	2	1	yes	

FIGURE 4 Comparison of the number of substituents in the 3 or 4 position and the mesomorphic properties

CONCLUSION

The synthesis of these two new series of biforked mesogens definitively demonstrates the high potential of these new kinds of mesogenic materials to exhibit mesomorphic polymorphism.[10] Taking into account that these materials are much more easy to synthesize than disc-like mesogens,[7] no doubt more extensive work will be done in the near future[9] in order to check more accurately the role of molecular design in relation to mesophase nature: lamellar, columnar, lamello-columnar and uniaxial or biaxial nematic behaviour. At least some preliminary conclusions have been reached in this paper about the relationship between the number, position and nature of the substituents. These conclusions will be used as a guide in our future synthetic work.

Acknowledgments

The authors are indebted to Dr. J. Malthete for DSC measurements and to Dr. L. Liebert for optical textural observations on the nematic phase.

References

1. J. Malthete and J. Collet, *Nouv. J. Chim.*, **9**, 151 (1985); H. Zimmermann, H. Poupko, R. Luz and J. Billard, *Z. Naturforsch. Teil A*, **40**, 149 (1985).
2. J. M. Lehn, J. Malthete and A. M. Levelut, *J. Chem. Soc. D*, 1794 (1985).
3. H. T. Nguyen, J. Malthete and C. Destrade, *Mol. Cryst. Liq. Cryst.*, **2**, 133 (1985).
4. H. T. Nguyen, C. Destrade, A. M. Levelut and J. Malthete, *J. Phys.* (*Paris*), **47**, 553 (1986).
5. J. Malthete, A. M. Levelut and H. T. Nguyen, *J. Phys.* (*Paris*) *Lett.*, **46**, L-875 (1985).
6. J, Malthete, L. Liebert, A. M. Levelut and Y. Galerne, *C. R. Acad.*, *Sci.*, *Paris*, *T. 303*, *Série II*, *n°12* 1073 (1986).

7. S. Chandrasekhar, S. Shadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977); C. Destrade, P. Foucher, H. Gasparoux, H. T. Nguyen, A. M. Levelut and J. Malthete, *Mol. Cryst. Liq. Cryst.*, **106**, 121 (1984).
8. L. Liebert, private communication.
9. S. Chandrashekar, *Mol. Cryst. Liq. Cryst.*, **124**, 1 (1985).
10. D. Guillon, A. Skoulios and J. Malthete, *Europhys. Lett.*, **3**, 67 (1987).
11. J. Malthete, H. T. Nguyen and A. M. Levelut, *J. Chem. Soc. Chem. Commun.*, 1548 (1986).