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J C Dubois, A. Zann. SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME NEW 4-4' DISUBSTITUTED BIPHENYLS. Journal de Physique Colloques, 1976, 37 (C3), pp.C3-35-C3-40. 10.1051/jphyscol:1976305 . jpa-00216488

**HAL Id: jpa-00216488**

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Submitted on 4 Feb 2008

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## SYNTHESIS AND MESOMORPHIC PROPERTIES OF SOME NEW 4-4' DISUBSTITUTED BIPHENYLS

J. C. DUBOIS and A. ZANN

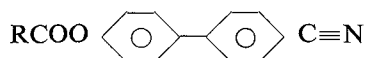
THOMSON-CSF, Laboratoire Central de Recherches  
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**Résumé.** — L'affichage par projection grand écran obtenu par effet thermo-optique sur les smectiques A ainsi que les effets de champ récemment étudiés rendent nécessaire la synthèse de produits aux caractéristiques adaptées. Seize esters de biphenyles para-bromés ou para-nitrilés ont été synthétisés. Les composés para-bromés présentent un polymorphisme smectique E, B ou/et A. Les composés para nitrilés présentent tous une phase nématique, les n-alkanoates à chaîne longue présentent en plus une phase smectique A utilisable dans les dispositifs à mémoire.

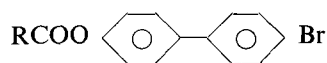
**Abstract.** — Smectic A mesophase with adequate characteristics is needed for displays using thermo-optic effect and for studies of field effect. Sixteen para-bromo-biphenyle-esters were synthesized. The para-bromo-compounds exhibit a smectic E, B and/or A polymorphism. The para-cyano compounds all show a nematic mesophase, the n-alkanoates with long aliphatic chain exhibit in addition a smectic A phase which is very interesting for storage displays.

**1. Introduction.** — Some applications, like storage displays, require stable and colourless smectic A mesophase. Gray [1] synthesized series of 4-alkyl or alkoxy 4'-cyano biphenyles, some of them exhibit  $S_A$  mesophases. Demus [2] prepared 4 alkanoyl 4'-alkyl-biphenyls which show  $S_E$  and  $S_A$  mesophases. So we investigated a new series of biphenyls :

4-cyano phenyl phenol esters :

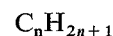


An intermediary step of the synthesis led us to the 4 bromo compounds

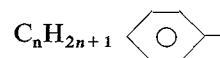


which were also characterized :

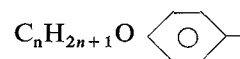
R is alkyl :



or 4-alkyl phenyl :



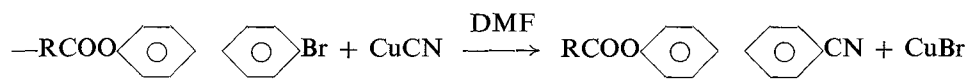
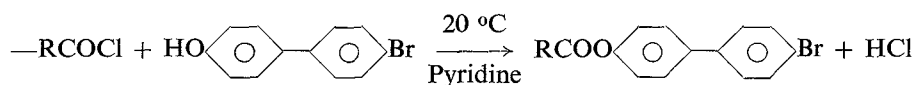
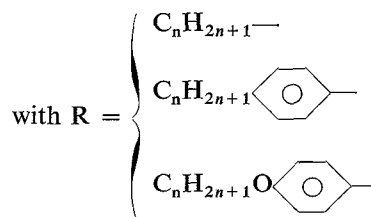
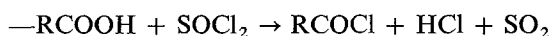
or 4'-alkoxy phenyl :



**2. Methods of preparation.** — The general method of preparation of these esters is given table I. It consists of an esterification of the 4-bromo 4'-phenyl-phenol by

TABLE I

*Synthesis of biphenyl esters*



the suitable acid chlorides. This step leads to the brominated compounds which are all mesomorphic.

The cyano compounds are obtained from the previous one by nucleophilic substitution of bromine, by means of cuprous cyanide. Copper is then complexed by ethylene diamine and the cyano diphenyl ester extracted with benzene.

Purification is achieved by chromatography on silica gel column with hexane : benzene eluant. If necessary, recrystallizations in ethanol are done.

### 3. Identification and characterization of mesophases.

— The temperatures and enthalpies of transitions were determined by differential scanning calorimetry (DSC 1B Perkin Elmer).

The textures of mesophases were observed between two cover slips with a polarizing microscope (Nacht) equipped with a heating and cooling stage (Mettler FP5).

Smectic mesophases were identified by means of contact method [3].

Isomorphies of unknown smectic phases with reference compounds were investigated.

3.1 4-BROMO OR 4-CYANO 4'-PHENYL PHENOL ALKANOATES (I). — 3.1.1 4-bromo compounds. — These compounds are listed table II. They all have a stable

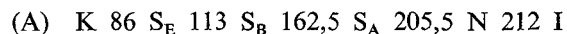
smectic B phase below 100 °C. The compounds with  $n = 5$  and  $n = 6$  have a stable smectic E phase before the smectic B. From  $n = 7$ , the E phase becomes monotropic and for  $n = 9$  it disappears completely. The temperatures of isotropic transitions are very near and located between 102,5 and 104,5 °C. Similarly, melting points are all between 68 and 76 °C.

The lengthening of the chain has very low influence upon the temperature range of mesomorphism but, inside this range, the smectic E phase disappears gradually for the benefit of the smectic B phase.

In this series, the texture of the smectic B phase is generally like *mosaic* with large domains (photo 1) and the smectic E one, like *striated mosaic* (photo 2).

On cooling, the isotropic — smectic B transitions of the two last compounds shows a *centred texture* (photo 3). When the temperature decreases, the centred droplets grow and attach themselves together; the obtained texture can be seen on photo 4.

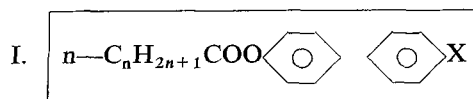
The identification of smectic E and B phases was done by studying their isomorphy with a reference compound : 4-methyl 2-propyl (4'-phenylbenzylidene-amino) cinnamate. This product was synthesized by Dr G. W. Gray <sup>(1)</sup> and has the following transitions :

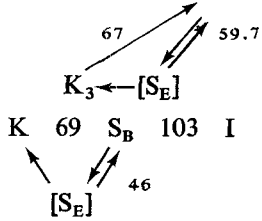
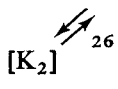


<sup>(1)</sup> We thanks Professor Gray for providing this compound.

TABLE II

Mesomorphic properties of biphenyl *n*-alkanoates



X	n	Transition temperatures							$\Delta H_f$ (kcal/mole)
—Br	5	K	70	S <sub>E</sub>	83	S <sub>B</sub>	103	I	
	6	K	68.5	S <sub>E</sub>	74	S <sub>B</sub>	104	I	
	7	K <sub>2</sub>	64.5	K <sub>1</sub>	76	S <sub>B</sub>	104.5	I	
—C≡N	8								
	9	K	73.5	S <sub>B</sub>	102.5	I			
	5	K <sub>1</sub>	52	K <sub>2</sub>	56	N	72	I	5.7
—C≡N	6	K	59	N	71	I			6.3
	7	K	78	I	75	N	[72]	K	8.3
	8	K <sub>1</sub>	42.5	S <sub>A</sub>	58	N	76	I	7.2
	9								4.9
	9	K	51	S <sub>A</sub>	76	N	76.5	I	8.3

The two smectic phases of compound  $n = 6$  are successively isomorphic with  $S_E$  and  $S_B$  phases of this cinnamate. The binary diagram of these two compounds is plotted on figure 1 n° 1.

The miscibility of compound  $n = 6$  with each other compounds of the same series was tested and their isomorphy verified. Two examples of binary diagrams are given figure 1 n° 2 (with  $n = 5$ ) and n° 3 (with  $n = 8$ ). When the smectic E phase is monotropic, the isomorphy is seen on cooling.

In this series, it is interesting to point out that the transition is direct from  $S_B$  to isotropy, which is very rare. Only one other compound showing such a transition is given elsewhere [8]: the di-*n*-hexadecanoyl fluorene.

3.1.2 4-cyano compounds. — These compounds are listed in table II. They all have a nematic phase, stable or monotropic. Compounds with  $n$  superior to seven exhibit in addition a smectic A phase. For  $n = 9$  the  $S_A$  phase is preponderant and the nematic phase reduced to half a degree. The melting points of this series are inferior to sixty degrees, except for the compound  $n = 7$  (melting point  $78^\circ\text{C}$ , nematic monotropic).

$S_A$  phases show focal conic textures and the nematic phases schlieren textures.

The  $S_A$  phase of compound  $n = 8$  was identified by Dr. J. Billard. This smectic is isomorphic with the  $S_A$  phase of 4-cyano 4'-octyloxy-biphenyl. We identified  $S_A$  phase of compound  $n = 9$  by its isomorphy with

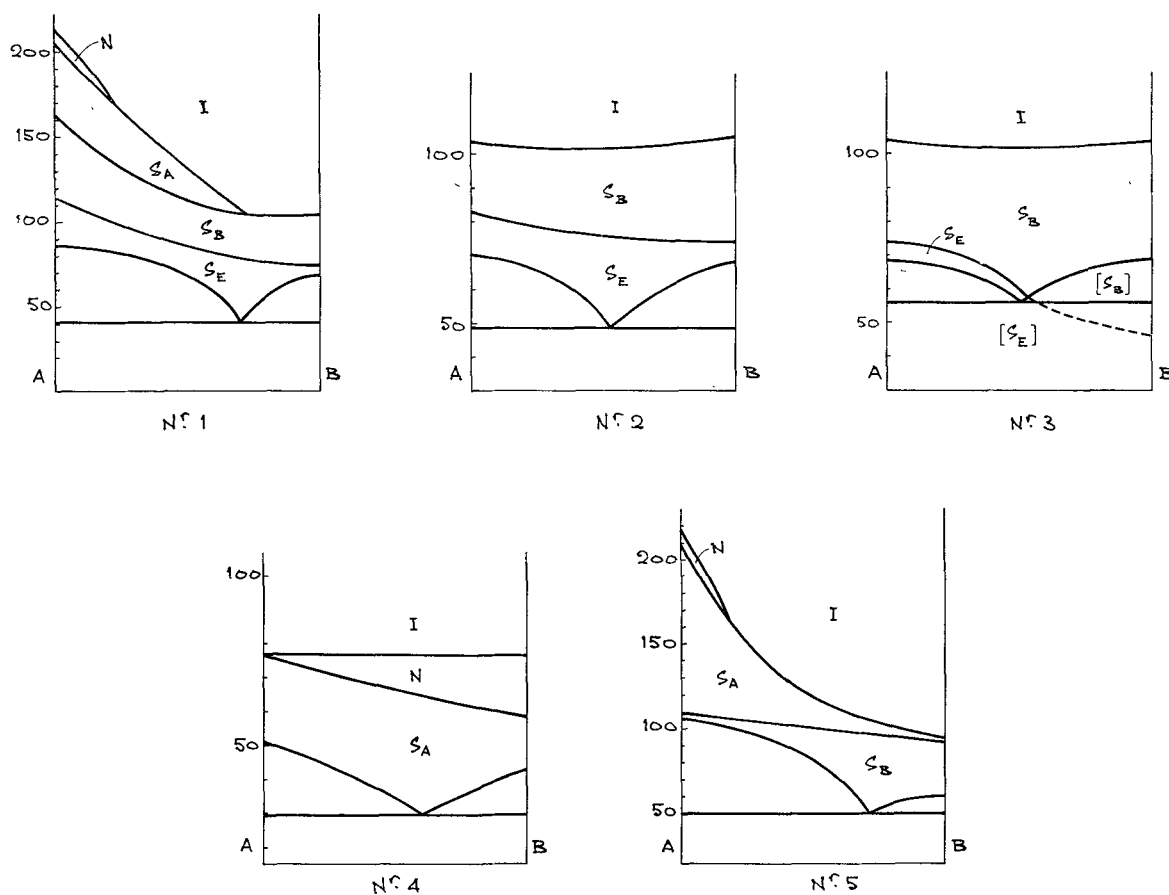
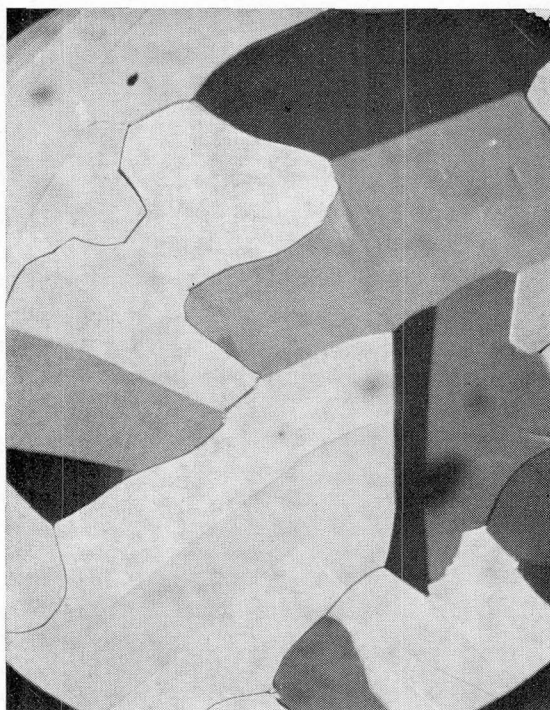
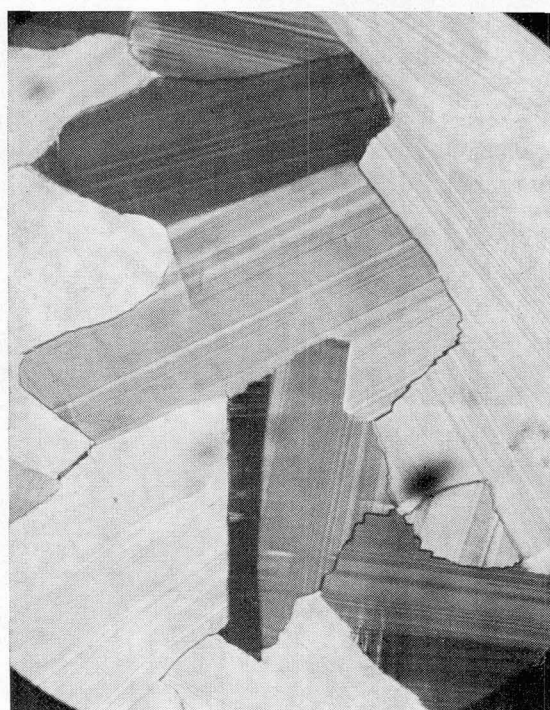


FIG. 1. — Isobaric diagrams of binary mixtures :

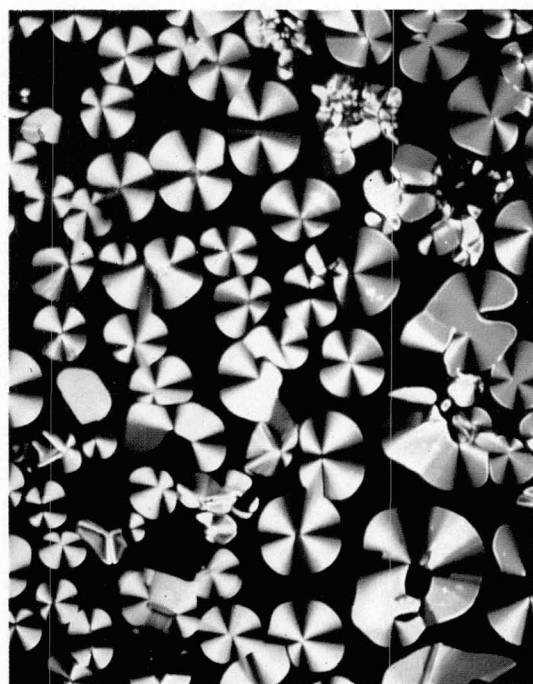
- n° 1 A : 2-methyl propyl 4(4' phenyl-benzylidene amino) cinnamate  
 B : 4 bromo phenyl phenol *n* heptanoate  
 n° 2 A : 4-bromo phenyl phenol *n*-hexanoate  
 B : 4-bromo phenyl phenol *n*-heptanoate  
 n° 3 A : 4-bromo phenyl phenol *n*-heptanoate  
 B : 4-bromo phenyl phenol *n*-nonanoate  
 n° 4 A : 4-cyano phenyl phenol *n*-decanoate  
 B : 4-cyano phenyl phenol *n*-nonanoate  
 n° 5 A : 4-bromo phenyl phenol 4' *n*-octyloxy benzoate  
 B : 4-*n*-pentyloxy benzylidene 4'-chloroaniline.



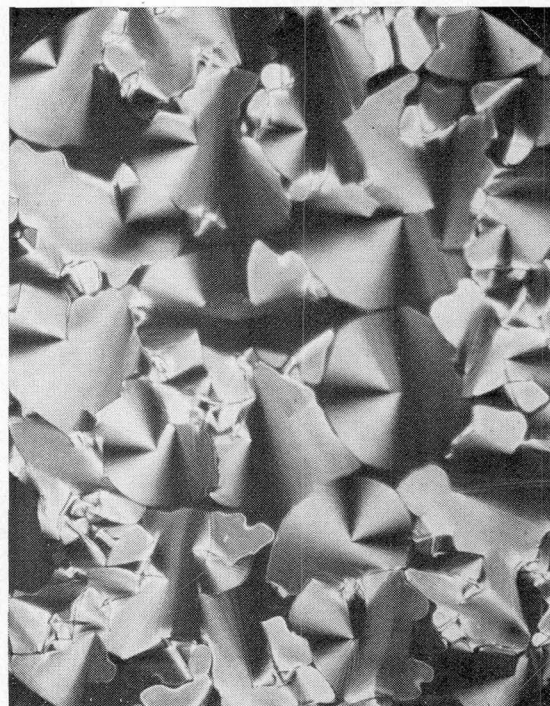
N° 1



N° 2



N° 3



N° 4

FIG. 2. — Photos taken by means of a polarizing microscope. Magnitude  $17 \times 10$ .

n° 1 : Mosaic texture of  $S_B$  phase.

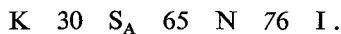
n° 2 : Striated mosaic texture of  $S_E$  phase.

n° 3 : Centred droplets texture of  $S_B$  phase near the isotropic transition on cooling.

n° 4 : Same texture than n° 3, far from the isotropic transition.

compound  $n = 8$ . Their diagram is plotted figure 1 n° 4. The experimental eutectic agrees with the theoretic one calculated from Schröder-Van Läär laws [4]. At the eutectic, concentrations are respectively 0.6 for  $n = 8$  and 0.4 for  $n = 9$ , in molar fractions.

The mesomorphic range is :



N. B. — The  $S_A$ -N transition of compound  $n = 8$  does not exhibit latent heat.

3.2 4-BROMO OR 4-CYANO PHENYL-PHENOL 4' n ALKYL BENZOATE. — Only one alkyl benzoate was prepared, the n-heptyl (Table III). The brominated compound has a smectic phase, not yet identified, and a nematic one.

The cyano compound is only nematic but on a very wide range, from 95,5 °C to 230 °C.




3.3 4-BROMO OR 4-CYANO PHENYL-PHENOL 4' n ALKOXY BENZOATES. — Two alkoxy benzoates were prepared, the n-butoxy and the n-octyloxy (Table III).

The brominated compound with  $n = 4$  is only smectic not yet identified ; the one with  $n = 8$  exhibits successively mesophases : smectic B, smectic A and nematic. The B to A transition is not visible on examination with a polarizing microscope ; on cooling, B pseudomorphoses the focal conics of A.  $S_B$  and  $S_A$  phases were identified by their isomorphy with  $S_B$  and  $S_A$  phases of the 4-n-pentyloxy benzylidene 4'-chloro aniline.

This product was already synthesized in the laboratory and identified by Dr. J. Billard [5].

TABLE III

## Mesomorphic properties of biphenyl-benzoates

II.		Transition temperatures						$\Delta H_f$			
$n-C_7H_{15}$  $COO$   X		$K_1$	109	$K_2$	133	S	194	N	200	I	
X		K	95.5	N	230	I					6.3
—Br											
—C≡N											













III.		Transition temperatures										$\Delta H_f$			
$n-C_nH_{2n+1}O$  $COO$   X															
X	$n$	K	147	S	228	I									
—Br	4	$K_3$	99	$K_2$	103	$K_1$	106	$S_B$	109	$S_A$	212.5	N	218	I	
—C≡N	4	K	120	N	270	I									7.6
	8	K	96.5	S	140	$S_A$	200	N	237	I					8.7

TABLE IV

## Dielectric anisotropy of nematic p-cyano biphenyl-esters

		Nematic range	Dielectric anisotropy (temperature)
I	$C_5H_{11}COO$   $C\equiv N$	K 56 N 72 I	$\Delta\epsilon_{max} (56^\circ) = 7.0$
	$C_6H_{13}COO$   $C\equiv N$	K 59 N 71 I	$\Delta\epsilon_{max} (64^\circ) = 5.3$
	$C_8H_{17}COO$   $C\equiv N$	$S_A$ 58 N 76 I	$\Delta\epsilon_{max} (64^\circ) = 4.0$
II	$C_7H_{15}$  $COO$   $C\equiv N$	K 95.5 N 230 I	$\Delta\epsilon (97^\circ) = 8.0$

The binary diagram is plotted figure 1 n° 5.

The two corresponding cyano-compounds are mesomorphic upon a wide range, larger than 100 °C. The compound with  $n = 4$  is only nematic, the one with  $n = 8$  exhibit a smectic phase not yet identified, a smectic A and a nematic phase. Between the *n*-heptyl benzoate and the *n*-octyloxy benzoate, we observe that the temperature range is quite the same but the nature of the mesomorphism different.

**4. Applications.** — Some of the compounds presented here may have applications in visualisation :

— Mixtures of nematic para-cyano compounds are interesting for devices based on field effect, as for example twisted nematic cell.

The dielectric anisotropy of these compounds was measured (Table IV). They are highly positive, the anisotropy decreasing with the lengthening of the chain.

— The thermo-optic storage display, first realized by Kahn [6] requires a colourless smectic A mesophase, followed by a nematic one. Hareng and Le Berre obtained very good results with a cell filled with a mixture of the 4-cyano phenyl phenol nonanoate described here and another biphenyl, first prepared by Dr. G. W. Gray, the 4-cyano 4'-octyl biphenyl.

— In addition, these cyano biphenyl esters exhibit an interesting property, recently studied by Hareng and Le Berre [7] : an electric field has an orientation effect on the  $S_A$  mesophase and, for example, induces an homeotropic state from a focal conic texture.

**5. Conclusion.** — In conclusion, sixteen para-substituted biphenyl esters were prepared, half of them para-brominated, the other half with a para cyano group.

The ester groups were : alkanates, alkyl benzoates or alkoxy benzoates :

— All the bromo-compounds exhibit smectic mesophases type E, B and/or A. Nematic mesophase appears for benzoates with long chain substituant.

— All the cyano-compounds show nematic phase ; benzoates have very wide nematic range but high melting points ; alkanates have shorter nematic range but lower melting points. Some of the latter compounds exhibit  $S_A$  mesophase which is very interesting for storage displays.

**Acknowledgement.** — The authors wish to thank Dr. J. Billard for very helpful discussions and F. Barre and J. C. Lavenu for technical assistance.

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