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## Liquid Crystals

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### Metallo-mesogens based on ortho-palladated polar imines: III. Influence of the polar group position

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## Metallo-mesogens based on ortho-palladated polar imines

### III. Influence of the polar group position

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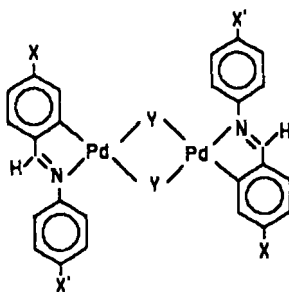
In order to study the influence of the molecular position of the polar group on the liquid crystal behaviour of palladium containing complexes, four series of complexes of the type  $\text{Pd}_2(\mu - Y)_2\{p\text{-}X\text{-C}_6\text{H}_3\text{-CH=N-C}_6\text{H}_4\text{-OC}_8\text{H}_{17}\}_2$  and  $\text{Pd}_2(\mu - Y)_2\{p\text{-C}_8\text{H}_{17}\text{O-C}_6\text{H}_3\text{-CH=N-C}_6\text{H}_4\text{-}X\}_2$ ;  $X$ : -H, -CH<sub>3</sub>, -OCH<sub>3</sub>, -Cl, -NO<sub>2</sub>, -CN and  $Y$ : -OOC.CH<sub>3</sub>, -Cl have been synthesized. A comparative study has revealed that the rigid central core is mainly responsible for the mesogenic behaviour of these complexes (acetato-bridged compounds do not form liquid crystals) and the polar group position only modifies this behaviour slightly. However, it has been observed that the nature of the anilinic ring substituent has a significant influence on the mesogenic properties of the chloro-bridged complexes.

#### 1. Introduction

The presence of mesogenic properties in molecules containing metal atoms in their structure has opened up great possibilities for both the design and the practical application of liquid crystals [1-4]. Palladium is among the most versatile metals used so far, with example of both mesogenic organometallic and coordination palladium containing complexes having been reported [2, 4-11].

An important part of our work with metallomesogenic compounds has been focused on the design, synthesis and chemical structure-mesogenic activity studies of ortho-palladated complexes [12-16]. One of our studies carried out with acetato- and chloro-bridged complexes derived from twelve polar 4-*n*-octyl-*N*-(4'-*X*-benzylidene)-anilines showed that the central structure of the molecule was principally responsible for their liquid crystal behaviour. It was found that the nature of the polar substituent played a secondary role [13]. However, as in the case of calamitic organic liquid crystals [17-18], the position of the polar substituents in the molecule could have a significant influence. The greater mobility of the anilinic ring together with the longer distance of the *para*-position of this ring from the central core may allow a more important participation of the different polar groups in the molecular interactions. As a result, changes in mesogenic behaviour such as the type of mesophase, mesophase range, etc., might be expected.

In this paper we report our results with regard to this. Four new series of acetato- and chloro-bridged ortho-palladated complexes have been synthesized and their



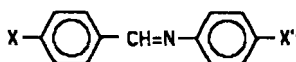
**SERIES IA :** Y: CH<sub>3</sub>COO; X: H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl, CN, NO<sub>2</sub>; X': OC<sub>8</sub>H<sub>17</sub>

**SERIES IB :** Y: CH<sub>3</sub>COO; X: OC<sub>8</sub>H<sub>17</sub>; X': H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl, CN, NO<sub>2</sub>

**SERIES IIA :** Y: Cl; X: H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl, CN, NO<sub>2</sub>; X': OC<sub>8</sub>H<sub>17</sub>

**SERIES IIB :** Y: Cl; X: OC<sub>8</sub>H<sub>17</sub>; X': H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl, CN, NO<sub>2</sub>

Sketch 1.



**SERIES A :** X: H, CH<sub>3</sub>, OCH<sub>3</sub>, Cl, CN[19], NO<sub>2</sub>[20]; X': OC<sub>8</sub>H<sub>17</sub>

**SERIES B :** X': OC<sub>8</sub>H<sub>17</sub>; X: H, CH<sub>3</sub>[21], OCH<sub>3</sub>, Cl[22], CN[23], NO<sub>2</sub>

Sketch 2.

mesogenic behaviour studied. These complexes allow us to study the influence of the molecular position of the polar group on liquid crystal behaviour. Furthermore, differences in mesogenic behaviour between the alkoxy series IA and the alkyl homologous series described in our previous paper [13] are also established. Although five of the twelve Schiff bases used as organic ligands have already been reported in the literature, all of them were synthesized and their liquid crystal properties are included in table 3 for comparisons. Comparative studies similar to those mentioned for palladium complexes were also carried out with the ligands.

## 2. Experimental

### 2.1. Synthesis of the ligands

All 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)anilines and the 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines with polar group -H, -CH<sub>3</sub>, -OCH<sub>3</sub> and -Cl, were synthesized by acetic acid catalysed condensation in absolute ethanol [24]. The 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines with strong electron withdrawing polar groups (-CN and -NO<sub>2</sub>) were synthesized by *p*-toluene sulphonic acid catalysed condensation in hot toluene, using a Dean Stark apparatus to remove the water [25]. These Schiff bases were characterized by C, H, N microanalysis and IR spectroscopy; satisfactory results were obtained.

### 2.2. Synthesis of the complexes

The four series of palladium containing compounds were obtained by methods already reported by us [12]. Analytical data and the most relevant IR data of these complexes are listed in tables 1 and 2.

Table 1. Analytical data (calculated values in parenthesis) and relevant IR data for the acetato-bridged complexes of series IA and IB.

Series	X	Analytical data			IR data		
		C	H	N	$\nu(X)/\text{cm}^{-1}$	$\nu^\dagger(\text{C}=\text{N}, \text{C}=\text{C}, \text{C}=\text{O})/\text{cm}^{-1}$	$\nu(\text{C}-\text{O})/\text{cm}^{-1}$
IA	H	58.10 (58.28)	6.22 (6.18)	2.80 (2.96)		1605, 1595, 1550, 1515	1270, 1220, 1060
	CH <sub>3</sub>	59.33 (59.96)	6.93 (6.88)	2.89 (2.80)		1620, 1600, 1585, 1550, 1515	1270, 1205, 1035
	OCH <sub>3</sub>	56.78 (57.19)	6.55 (6.21)	2.68 (2.78)	‡	1615, 1600, 1575, 1545, 1515	1275, 1235, 1045, 1035
	Cl	54.55 (54.34)	5.76 (5.56)	2.81 (2.76)	835	1615, 1595, 1565, 1540, 1515	1250, 1205, 1030
	NO <sub>2</sub>	53.93 (53.23)	5.89 (5.45)	5.55 (5.40)	1345	1615, 1590, 1535, 1525, 1515	1265, 1210, 1030
	CN	58.47 (57.77)	5.59 (5.67)	5.58 (5.62)	2240	1610, 1595, 1575, 1535, 1510	1260, 1205, 1050
IB	H	58.17 (58.28)	6.39 (6.18)	3.29 (2.96)		1615, 1595, 1580, 1555, 1540	1275, 1205, 1040
	CH <sub>3</sub>	59.07 (59.96)	6.42 (6.88)	2.87 (2.80)		1615, 1600, 1580, 1550, 1510	1270, 1210, 1035
	OCH <sub>3</sub>	57.81 (57.19)	6.29 (6.21)	2.83 (2.78)	‡	1610, 1580, 1560, 1540, 1510	1270, 1210, 1050, 1040
	Cl	54.93 (54.34)	5.97 (5.56)	2.85 (2.76)	845	1605, 1580, 1555, 1545, 1535	1270, 1210, 1035
	NO <sub>2</sub>	52.89 (53.23)	5.77 (5.45)	5.40 (5.40)	1355	1605, 1595, 1570, 1525, 1510	1270, 1205, 1035
	CN	56.72 (57.77)	5.68 (5.67)	5.72 (5.62)	2215	1605, 1585, 1540, 1505	1265, 1210, 1030

† Overlap of the (C=N), (C=C) and (C=O) absorptions precludes unequivocal assignment of these bands.

‡ Absorption of the O-CH<sub>2</sub>R band in the same range precludes the unequivocal assignment of this band.

Table 2. Analytical data (calculated values in parenthesis) and relevant IR data for the chloro-bridged complexes of series IIA and IIB.

Series	X	Analytical data			IR data		$\nu(\text{C-O})/\text{cm}^{-1}$
		C	H	N	$\nu(\text{X})/\text{cm}^{-1}$	$\nu^\dagger(\text{C=N, C=C})/\text{cm}^{-1}$	
IIA	H	55.71 (56.00)	6.05 (5.83)	3.11 (3.11)		1606, 1586, 1550, 1503	1244, 1040
	CH <sub>3</sub>	56.75 (56.90)	6.38 (6.09)	3.04 (3.02)		1605, 1581, 1544, 1504	1248, 1042
	OCH <sub>3</sub>	55.68 (55.00)	6.14 (5.89)	2.92 (2.92)	‡	1607, 1581, 1547, 1503	1216, 1037
	Cl	52.05 (52.02)	5.38 (5.21)	2.95 (2.89)	828	1606, 1585, 1565, 1539, 1503	1251, 1040
	NO <sub>2</sub>	50.76 (50.92)	5.27 (5.10)	5.25 (5.66)	1334	1607, 1581, 1560, 1514, 1504	1248, 1040
	CN	55.28 (55.58)	5.24 (5.31)	5.91 (5.89)	2222	1606, 1582, 1503	1252, 1041
IIB	H	55.42 (56.00)	5.99 (5.83)	2.96 (3.11)		1684, 1587, 1543	1264, 1030
	CH <sub>3</sub>	56.74 (56.90)	6.45 (6.09)	2.95 (3.02)		1607, 1575, 1529, 1502	1268, 1043
	OCH <sub>3</sub>	55.24 (55.00)	6.20 (5.89)	2.95 (2.92)	‡	1607, 1587, 1543, 1503	1261, 1046
	Cl	52.18 (52.02)	5.36 (5.21)	2.87 (2.89)	829	1595, 1582, 1539	1265, 1025
	NO <sub>2</sub>	50.73 (50.92)	5.19 (5.10)	5.73 (5.66)	1342	1580, 1571, 1521	1239, 1029
	CN	55.22 (55.58)	4.79 (5.31)	5.82 (5.89)	2227	1596, 1585, 1529	1271, 1025

‡ Overlap of the (C=N), (C=C) absorptions precludes unequivocal assignment of these bands.

‡ Absorption of the O-CH<sub>2</sub>R band in the same range precludes the unequivocal assignment of this band.

## 2.3. Techniques

The melting points, transition temperatures and enthalpies of transition were determined using a Perkin-Elmer DSC-2. The heating rate was 10 K/min and the apparatus was calibrated by measuring the known melting point and heat of fusion of indium (429.6 K, 28.1 J g<sup>-1</sup>). The optical observations were made using a Meiji polarizing microscope equipped with a Mettler FP 82 hot stage and a FP 80 central processor. The identification of the products was carried out by the usual methods: elemental analysis (Perkin-Elmer 240B Microanalyser), IR (Perkin-Elmer 1600 FT) and <sup>1</sup>H NMR (Varian XL-200).

## 3. Results and discussion

## 3.1. Mesogenic behaviour of the ligands

The thermal and thermodynamic data for 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)-anilines (series A) and 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines (series B) used as organic ligands are summarized in table 3. Figure 1 shows a comparative study of the

Table 3. Thermal and thermodynamic data for 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)anilines (Series A) and 4-*X*-*N*-(4'-*n*-octyloxybenzylidene) anilines (series B).

Series	<i>X</i>	Transition	<i>T</i> /°C	$\Delta H$ /kJ mol <sup>-1</sup>
A	H	C-I	70.9	40.18
		C-I	78.0	38.68
	CH <sub>3</sub>	I-N†	77.4	-0.88
		C-I	104.3	48.56
	OCH <sub>3</sub>	I-N†	99.1	-0.13
		C-S <sub>B</sub>	93.7	32.68
		S <sub>B</sub> -S <sub>A</sub>	100.2	3.12
	Cl	S <sub>A</sub> -I	110.8	6.33
		C-S <sub>A</sub>	75.2	27.15
		S <sub>A</sub> -N	88.9	0.30
	CN	N-I	110.0	0.65
		C-S <sub>A</sub>	66.1	32.78
		S <sub>A</sub> -N	79.5	0.10
	NO <sub>2</sub>	N-I	88.2	0.33
C-I		56.3	36.72	
C-N		65.7	38.33	
B	H	N-I	72.8	1.02
		N-S <sub>A</sub> †	64.3	-2.32
	CH <sub>3</sub>	S <sub>A</sub> -S <sub>B</sub> †	56.7	-1.63
		C-I	106.2	48.82
	OCH <sub>3</sub>	I-N†	102.4	-0.13
		C-S <sub>B</sub>	65.6	26.88
		S <sub>B</sub> -S <sub>A</sub>	86.8	3.29
	Cl	S <sub>A</sub> -I	97.3	5.77
		C-N	81.2	36.78
	CN	N-I	97.0	0.45
		C-I	90.4	36.84
	NO <sub>2</sub>	I-N†	84.1	-0.47
		N-S <sub>A</sub> †	82.3	-0.27

† Monotropic transition.

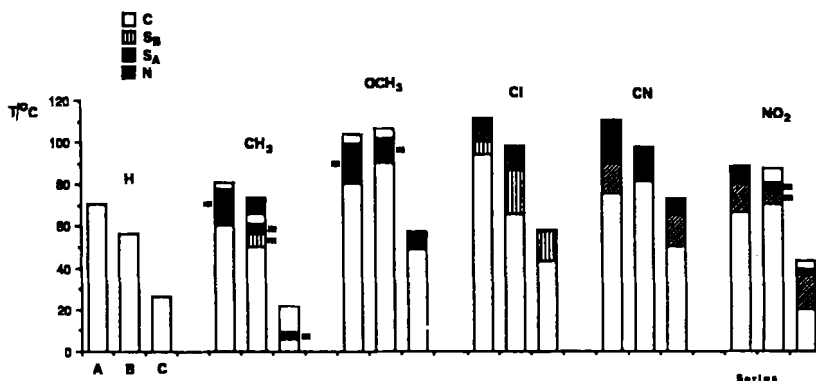


Figure 1. Transition temperatures for the 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)anilines (series A), 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines (series B) and 4-*n*-octyl-*N*-(4'-*X*-benzylidene)anilines (series C). (With the exception of the monotropic transitions, all of the temperatures correspond to heating scans.) (m, monotropic transition.)

liquid crystal behaviour of series A and B together with the 4-*n*-octyl-*N*-(4'-*X*-benzylidene)anilines (series C) reported previously by us [13]. As we can see, a similar influence of the different polar substituents exists in all three series. While the chloro-group favours S<sub>A</sub> and S<sub>B</sub> mesophases and the methoxy group a nematic one, the strong electron withdrawing groups, nitro and cyano, give rise to nematic and S<sub>A</sub> mesophases. In the absence of substituents (*X* or *X'*: -H) no liquid crystal behaviour was observed.

As expected, the alkyl-Schiff bases have the lowest melting points but the influence of the polar group on the melting points is different in each series. However, the influence of these polar substituents on the clearing points is similar in the three series and the order of terminal group efficiency in promoting nematic phases for the three series are very similar to those reported [26]. It is noteworthy that the strong electron withdrawing groups (-NO<sub>2</sub> and -CN) give rise to better liquid crystal properties (lower melting points, enantiotropic mesophases and/or broader mesophase ranges) when they are placed on the aldehydic ring. Likewise, the cyano group gives rise to a more stable mesophase and a broader mesophase range than the strong electron withdrawing nitro group. This can be attributed to the well-known tendency of the cyano group to antiparallel association [27] which should stabilize molecular interactions.

### 3.2. Study of the palladium complexes

The spectroscopic data for the complexes (IR and <sup>1</sup>H NMR) are coincident with those obtained for similar compounds [12, 13, 28]. From these results we deduce (i) that they are dinuclear, (ii) the *trans*-isomer is the only isomer present, and (iii) the acetato-bridged complexes are non-planar and the chloro-bridged derivatives planar [13].

#### Mesogenic behaviour

Tables 4 and 5 summarize the transition phases observed for the palladium complexes described here. Once again, the appearance of a mesophase was not observed with the book-shaped acetato-complexes derived from Schiff bases, but with the planar chloro-compounds a mesophase appeared [13].

Table 4. Thermal and thermodynamic data for acetato-bridged complexes derived from 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)anilines (series IA) and 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines (series IB).

Series	X	Transition	T/°C	ΔH/kJ mol <sup>-1</sup>
IA	H	C-I	135.6	41.78
	CH <sub>3</sub>	C-I	178.7	61.24
	OCH <sub>3</sub>	C-I	163.6	59.51
	Cl	C-I	186.0	64.22
	CN	C-I	137.3	38.63
	NO <sub>2</sub>	C-I	177.6	55.66
IB	H	C-I	176.0	45.26
	CH <sub>3</sub>	C-I	197.0	48.67
	OCH <sub>3</sub>	C-I	190.6	45.13
	Cl	C-I	204.0	38.04
	CN	C-I	186.2	30.89
	NO <sub>2</sub>	C-C' C'-I	173.4 191.6	17.12 32.13

Table 5. Thermal and thermodynamic data for the chloro-bridged complexes derived from 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)anilines (series IIA) and 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines (series IIB).

Series	X	Transition	T/°C	ΔH/kJ mol <sup>-1</sup>
IIA	H	C-C'	160.1	4.58
		C'-S <sub>A</sub>	184.3	31.71
		S <sub>A</sub> -I	222.3	4.58
	CH <sub>3</sub>	C-S <sub>A</sub>	159.7	32.70
		Decomp.	256	
	OCH <sub>3</sub>	C-S <sub>A</sub>	172.1	89.11
		Decomp.	260	
	Cl	C-S <sub>A</sub>	162.4	25.41
		Decomp.	268	
	CN	C-S <sub>A</sub>	210.2	37.39
		Decomp.	267	
	NO <sub>2</sub>	C-S <sub>A</sub>	174.0	66.71
Decomp.		266		
IIB	H	C-I	203.8	58.58
		C-C'	107.8	69.93
		C'-S <sub>A</sub> Decomp.	144.5 261	25.50
	OCH <sub>3</sub>	C-C'	168.6	29.30
		C'-S <sub>A</sub> Decomp.	188.7 264	29.94
		C-I	171.7	48.92
	Cl	C-S <sub>A</sub> Decomp.	272	
		C-C'	173.8	14.06
		C'-N Decomp.	207.5 247	31.65
	NO <sub>2</sub>	C-S <sub>A</sub> Decomp.	231.3 262	27.53



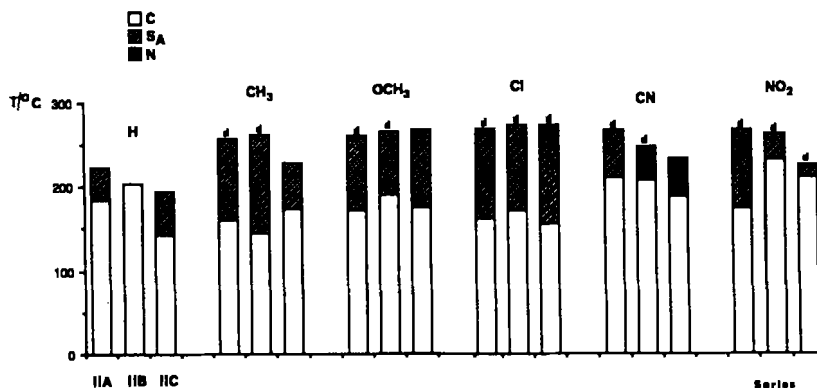


Figure 2. Transition temperatures for the chloro-bridged complexes derived from 4-*n*-octyloxy-*N*-(4'-*X*-benzylidene)anilines (series IIA), 4-*X*-*N*-(4'-*n*-octyloxybenzylidene)anilines (series IIB) and 4-*n*-octyl-*N*-(4'-*X*-*n*-octylbenzylidene)anilines (series IIC). (d, the complex decomposes on reaching this temperature.)

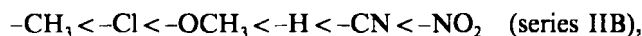
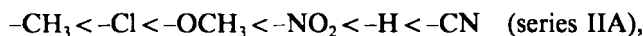
A comparative study of the properties of the acetato-bridged series IA and IB reveals a similar sequence of polar groups for the melting points in both series:  $-H < -CN < -OCH_3 < -NO_2 < -CH_3 < -Cl$ ; this indicates a similar participation of these polar groups in the molecular interactions in the solid phase in both series. All of these compounds pass to the isotropic liquid without decomposition.

The complexes derived from polar aldehydes (series IA) melt 20–50°C lower than their homologues in series IB. However, these differences were not observed for the chloro-complexes. Both kinds of palladium complexes studied here ( $Y: -OOC.CH_3$  and  $-Cl$ ) show high transition enthalpies of melting: 30–64 kJ mol<sup>-1</sup> for acetato-bridged complexes and 25–89 kJ mol<sup>-1</sup> for the chloro-bridged complexes (see tables 4 and 5) but no polar group-Δ*H* relationship can be established.

Regarding the liquid crystal behaviour of the chloro-bridged complexes all of them exhibit mesogenic behaviour with the exception of that derived from 4-*n*-octyloxybenzylideneaniline. The *S<sub>A</sub>* phase formed by most of these complexes showed characteristic melinic and homeotropic textures on heating and a fan-shaped texture for the H-complex in series IIA was also observed on cooling. The nematic phase that occurred in the cyano-complex of series IIB, exhibited a clear marbled texture on heating.

As reported for other ortho-palladated complexes of this kind [12, 13], the mesophases have a high viscosity and in many cases, the solid obtained on cooling retained the previous mesophase texture.

Figure 2 shows a comparative study of the liquid crystal properties of the chloro-bridged complexes of series IIA and IIB together with those of series IIC derived from 4-*n*-octyl-*N*-(4'-*X*-benzylidene)anilines [13]. A fairly similar sequence of polar groups-melting points is observed in both alkoxy-series



in which strong electron withdrawing groups give rise to the highest melting points as observed in series IIC. However, these sequences are not similar to that observed for the acetato-complexes, which shows that the influence of the polar group on the stabilization of the solid state depends on the central core of the molecule.

Practically all the chloro-complexes described here decomposed (as observed by DSC and microscopy) within the range 240–270°C which determines their mesophase stability. In general the compounds of series IIA show the broadest liquid crystal mesophase range, but no clear polar group-mesophase range relationship can be established. The broad mesophase range (higher than 100°C) exhibited by compounds with the chloro-group in the three series is noteworthy.

The results, so far, show that with these ortho-palladated imine complexes, the nature of the central core is again mainly responsible for the liquid crystal properties: namely the appearance of a mesophase and the molecular arrangement in it (basically  $S_A$ ), and that the position of the polar group in the molecule does not play an important role. However, it should be pointed out that the nature of the anilinic substituent has a significant influence on the molecular interactions in these compounds. Thus, the absence of a substituent ( $X'$ : -H) prevents liquid crystal behaviour. Furthermore, strong electron withdrawing groups ( $X'$ : -NO<sub>2</sub> and -CN) give rise to the highest melting points, the shortest mesophase ranges or a less ordered nematic phase (see figure 2), and lead to the most significant differences between series IIA and IIB. It is noteworthy that the negative effect of these two groups was also observed in series IIC, in which these complexes show a similar liquid crystal behaviour to that shown by the corresponding homologues in series IIB. However, the destabilizing influence of these groups, which can be attributed to electronic repulsions [13], is practically cancelled out when the *n*-octyloxy chain is present in the anilinic ring (series IIA). The electron pair present in this chain increases the molecular interactions in both the solid and the mesophase state, and lessens the influence of the polar groups in such a way that very similar behaviour is observed for the members of series IIA.

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