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# Mesogenic behaviour of two series of orthopalladated polar imine derivatives and their organic ligands (II)

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One series of 4-*n*-octyl-*N*-(4-*X*-benzylidene)anilines and two series of polar orthopalladated complexes derived from these of type $Pd_2(\mu\text{-}Y)_2\{p\text{-}X\text{-}C_6H_3\text{-}CH{=}N\text{-}C_6H_4\text{-}C_8H_{17}\}_2$; *X*: -H, -F, -Cl, -Br, $-NO_2$, -CN, $-CH_3$, $-OCH_3$, $-CF_3$, $-COOCH_3$, $-OCOCH_3$ and $-OCOC_6H_5$; *Y*: -OAc and -Cl; have been synthesized and their mesogenic properties studied. In the polar Schiff bases used as organic ligands, the polar end group determines both the presence of the mesophase and the type of mesophase exhibited. In the complexes, however, it is the central structure of the molecule that practically always determines mesogenic behaviour. No acetato-bridged complex is mesogenic. All the chloro-bridged complexes, however, show mesogenic behaviour. All these compounds show smectic A mesophases with the exception of the CN compound, which only exhibits a nematic mesophase.

## 1. Introduction

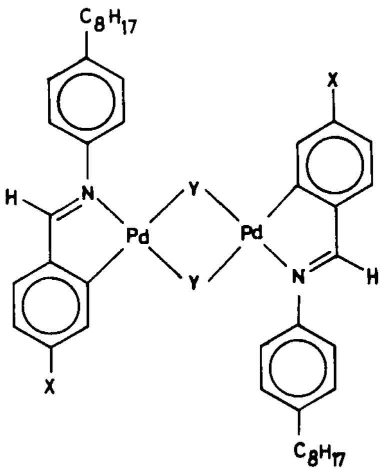
The first mesogenic orthopalladated complexes were reported by Ghedini *et al.* [1, 2]. The organic ligands of these compounds were azobenzene derivatives. Recently, we have described the mesogenic properties of twelve similar compounds derived from Schiff bases [3]. These compounds provide a basis for studying the influence of (*a*) terminal chains, (*b*) substitution on the imine-carbon and (*c*) the nature of the bridges between the metallic centres, on the mesogenic properties.

Continuing our work on the structure–activity relations in organometallic compounds with palladium, we describe in this paper the synthesis and characterization of two new series of orthopalladated imine derivatives with different polar groups in their structure. This allows us to study the influence of the polarity of the terminal substituents on mesogenic properties for the series

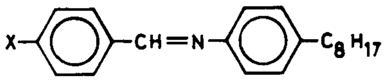
(I) di-$\mu$-acetate-bis-(4-*n*-octyl-*N*-(4-X-benzylidene)aniline $C^2$, N) palladium(II) $[Pd_2(\mu\text{-}OAc)_2L_2]$ and
(II) di-$\mu$-chloro-bis-(4-*n*-octyl-*N*-(4-X-benzylidene)aniline $C^2$, N) palladium(II) $[Pd_2(\mu\text{-}Cl)_2L_2]$.

All the complexes synthesized have as organic ligand 4-*n*-octyl-*N*-(4-X-benzylidene)aniline which introduces the polar group.

All the Schiff bases were synthesized and characterized by us, and, with the exception of the imines with X: $-OCH_3$ [4] and -CN [5], it is the first time they have been described in the literature.



X: H, F, Cl, Br, CN, $NO_2$, $CH_3$, $OCH_3$, $CF_3$, $OCOCH_3$, $OCOC_6H_5$, $COOCH_3$.
Y: OAc, Cl.



X: H, F, Cl, Br, CN, $NO_2$, $CH_3$, $OCH_3$, $CF_3$, $OCOCH_3$, $OCOC_6H_5$, $COOCH_3$.

## 2. Experimental

### 2.1. *Synthesis of the ligands*

With the exception of the imines with groups *X*: $-OCOCH_3$ and $-OCOC_6H_5$, all of these were synthesized by acetic acid catalyzed condensation, as described in the literature [3, 6]. The Schiff bases with *X*: $-OCOCH_3$ and $-OCOC_6H_5$ were obtained by esterification of the 4-*n*-octyl-*N*-(4-hydroxybenzylidene)aniline with the corresponding acid chloride in pyridine.

### 2.2. *Synthesis of the complexes*

The two series of complexes were obtained by methods similar to others described in the literature [3, 7, 8].

### 2.3. *Techniques*

The melting points, transition temperatures and enthalpies of transition were determined using a Perkin–Elmer DSC-2 differential scanning calorimeter. 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 $g^{-1}$). The optical observations were made using a MEIJI polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor.

The identification of the products was carried out by the usual methods: Perkin–Elmer 240B microanalyzer, IR Perkin–Elmer 599, $^1H$-NMR (Brucker WP-80-CW) and the molecular weights were measured with a Knauer vapour pressure osmometer.

## 3. Results and discussion

### 3.1. *Mesogenic behaviour of the ligands*

The thermal and thermodynamic data for the twelve 4-*n*-octyl-*N*-(4-X-benzylidene)-anilines used as organic ligands are gathered in table 1 and their mesogenic properties

Table 1. Thermal and thermodynamic data for the 4-*n*-octyl-*N*-(4-X-benzylidene)anilines.

| *X* | Transition | Temperature K | $\Delta H$ kJ mol$^{-1}$ |
|---|---|---|---|
| H | C-I | 299·2† | |
| $CH_3$ | C-I | 296·1† | |
| | I-N‡ | 282·2† | |
| F | C-I | 314·0 | 36·71 |
| Cl | C-$S_B$ | 316·1 | 32·45 |
| | $S_B$-I | 330·7 | 7·85 |
| Br | C-$S_B$ | 320·4 | 31·22 |
| | $S_B$-I | 341·6 | 8·14 |
| $NO_2$ | C-I | 315·7 | 33·47 |
| | I-N‡ | 315·0† | |
| | N-$S_A$‡ | 309·4† | |
| CN | C-N§ | 338·3 | 37·42 |
| | N-I | 345·2 | 0·75 |
| | N-$S_A$‡ | 337·8† | |
| | C-$S_A$¶ | 317·3 | 21·15 |
| | $S_A$-N | 335·5 | 0·10 |
| | N-I | 344·3 | 1·11 |
| $OCH_3$ | C-N | 321·6 | 21·15 |
| | N-I | 330·4 | 0·59 |
| $CF_3$ | C-$S_B$ | 302·6 | 27·42 |
| | $S_B$-I | 318·5 | 8·02 |
| $OCOCH_3$ | C-N | 327·9 | 28·88 |
| | N-I | 339·1 | 0·64 |
| $OCOC_6H_5$ | C-N | 372·7 | 46·12 |
| | N-I | 391·8 | 0·63 |
| $COOCH_3$ | $C_1$-$C_2$ | 351·3 | 4·71 |
| | $C_2$-I | 368·4 | 32·62 |
| OH | $C_1$-$C_2$ | 381·3 | 5·64 |
| | $C_2$-I | 425·8 | 43·98 |

† Optical microscopic data.
‡ Monotopic transition.
§ Data obtained in the first scan.
¶ Data obtained in the second scan.

(types and mesophases ranges) are represented in figure 1. The behaviour of these Schiff bases is very similar to that observed for the other imines with these polar groups described in the literature [4, 5]: low melting points and narrow mesophase ranges. As we can observe, the polar groups whose dipole moment characteristics (strength and direction) increase the axial dipole moment of the molecule give rise to the most ordered mesophases (smectic A and B). However, the groups with weak dipole moments, those which form an angle with the $C_{Ar}$–$X$ direction and/or are sterically hindered, only give rise to a nematic mesophase or, in some cases, no mesophase at all (*X*: $-COOCH_3$).

It can also be observed that the groups *X*: –CN and $-NO_2$, with the strongest dipole moments, show a smectic A mesophase, less ordered than the smectic B exhibited by the Schiff bases with groups *X*: –Cl, –Br and $-CF_3$.

In both groups the strong electron-withdrawing character results in interactions with different parts of other molecules and consequently in different molecular overlap. This overlap favours a nematic or bilayer arrangement rather than the monolayer that the imines seem to adopt with groups *X*: –Cl, –Br and $-CF_3$, as shown by Seurin *et al.* [9] with X-Ray studies of some 4-X-*N*-(4-*n*-alkoxybenzylidene)anilines (*X*: –Cl, –Br and –CN).

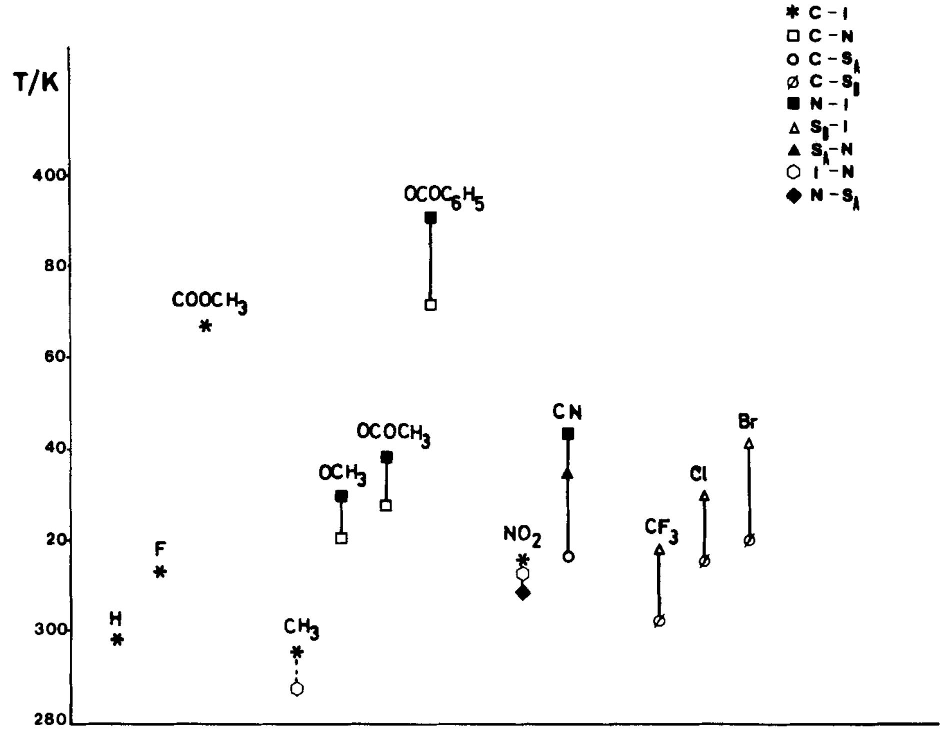


Figure 1. Transition temperatures of the 4-*n*-octyl-*N*-(4-X-benzylidene)anilines).

Table 2. Thermal and thermodynamic data of the recrystallized acetato-bridged complexes $[Pd_2(\mu\text{-}OAC)_2L_2]$.

| *X* | Transition | Temperature K | $\Delta H$ kJ mol$^{-1}$ |
|---|---|---|---|
| F | C–I | 437·5 | 25·02 |
| Cl | $C_1$–$C_2$ | 370·0 | 60·38 |
|  | $C_2$–I | 448·4 | 25·72 |
| Br | C–I | 444·7 | 25·22 |
| $NO_2$ | C–I | 406·9 | 30·65 |
| CN | C–I | 435·5 | 22·44 |
| $CF_3$ | C–I | 417·2 | 18·07 |
| $OCOCH_2$ | C–I | 419·2 | 33·87 |
| $OCOC_6H_5$ | C–I | 431·1 | 52·86 |
| $COOCH_3$ | C–I | 430·9 | 12·42 |

### 3.2. *Mesogenic behaviour of the complexes*

None of the acetato-bridged complexes studied show mesogenic behaviour. Their transition temperatures and enthalpies are summarized in table 2. However, all of the chloro-bridged complexes form liquid crystals and their properties are listed in table 3 and represented in figure 2. With the exception of the complex with the group *X*: –CN, which is the only one that shows a nematic phase, in all compounds a smectic A phase is formed as happens with the Schiff-base cyclopalladated complexes described by us in a previous paper [3]. This mesogenic behaviour is, however,

Table 3. Thermal and thermodynamic data of the chloro-bridged complexes $[Pd_2(\mu\text{-}Cl)_2L_2]$.

| *X* | Transition | Temperature K | $\Delta H$ kJ mol$^{-1}$ |
|---|---|---|---|
| H | $C_1$-$C_2$ | 375·8 | 15·40 |
| | $C_2$-$S_A$ | 415·1 | 50·76 |
| | $C_3$-$S_A$† | 438·8 | 1·38 |
| | $S_A$-I | 466·9 | 4·83 |
| F | C-$S_A$ | 431·8 | 39·28 |
| | $S_A$-I (decomp.) | 545·1 | |
| Cl | $C_1$-$C_2$ | 413·8 | 13·28 |
| | $C_2$-$S_A$ | 428·2 | 18·30 |
| | Decomp. | 546·0 | |
| Br | C-$S_A$ | 447·1 | 32·61 |
| | Decomp. | 544·0 | |
| CN | C-N | 461·5 | 20·05 |
| | N-I | 506·3 | 0·19 |
| $NO_2$ | C-$S_A$ | 483·4 | 60·34 |
| | Decomp. | 497·0 | |
| $CH_3$ | C-$S_A$ | 445·6 | 37·82 |
| | $S_A$-I (decomp.) | 501·5 | |
| $OCH_3$ | $C_1$-$C_2$ | 398·4 | 13·66 |
| | $C_2$-$S_A$ | 448·6 | 38·08 |
| | $S_A$-I (decomp.) | 538·7 | |
| $CF_3$ | C-$S_A$ | 480·3 | 32·58 |
| | $S_A$-I (decomp.) | 557·0 | |
| $OCOCH_3$ | $C_1$-$C_2$ | 420·8 | 25·15 |
| | $C_2$-$S_A$ | 427·4 | 11·15 |
| | $S_A$-I (decomp.) | 539·9 | |
| $OCOC_6H_5$ | $C_1$-$C_2$ | 408·0 | 40·18 |
| | $C_2$-$S_A$ | 477·8 | 45·93 |
| | Decomp. | 561·0 | |
| $COOCH_3$ | $C_1$-$C_2$ | 372·5 | 5·15 |
| | $C_2$-$S_A$ | 457·0 | 26·75 |
| | $S_A$-I (decomp.) | 522·0 | |

† Only in the first scan.

different from that observed in the closely analogous azocomplexes studied by Ghedini *et al.* [1, 2, 10], which principally show nematic phases.

In general, these complexes have mesophase ranges higher than 50°C, but they are not very stable thermally, so most of them decompose before melting or during the transition to the isotropic liquid.

The chloro-bridged compounds with groups *X*: $-H$, $-Cl$, $-OCH_3$, $-OCOCH_3$, $-OCOC_6H_5$ and $-COOCH_3$ show crystalline polymorphism. The complex with group *X*: $-H$, apart from a crystal–crystal transition $C_1$–$C_2$, shows two different solid arrangements at the same time, which melt at different temperatures:

$$\begin{tikzcd}
C_1 \arrow[r, "375\cdot8\,K"] & C_2 \arrow[r, "415\cdot1\,K"] \arrow[d, "*"'] & S_A \arrow[r] \arrow[ll, bend right] \\
& C_3 \arrow[ur, "438\cdot8\,K"'] &
\end{tikzcd}$$

*At temperatures between 415·1 K and 438·8 K only in the first scan.

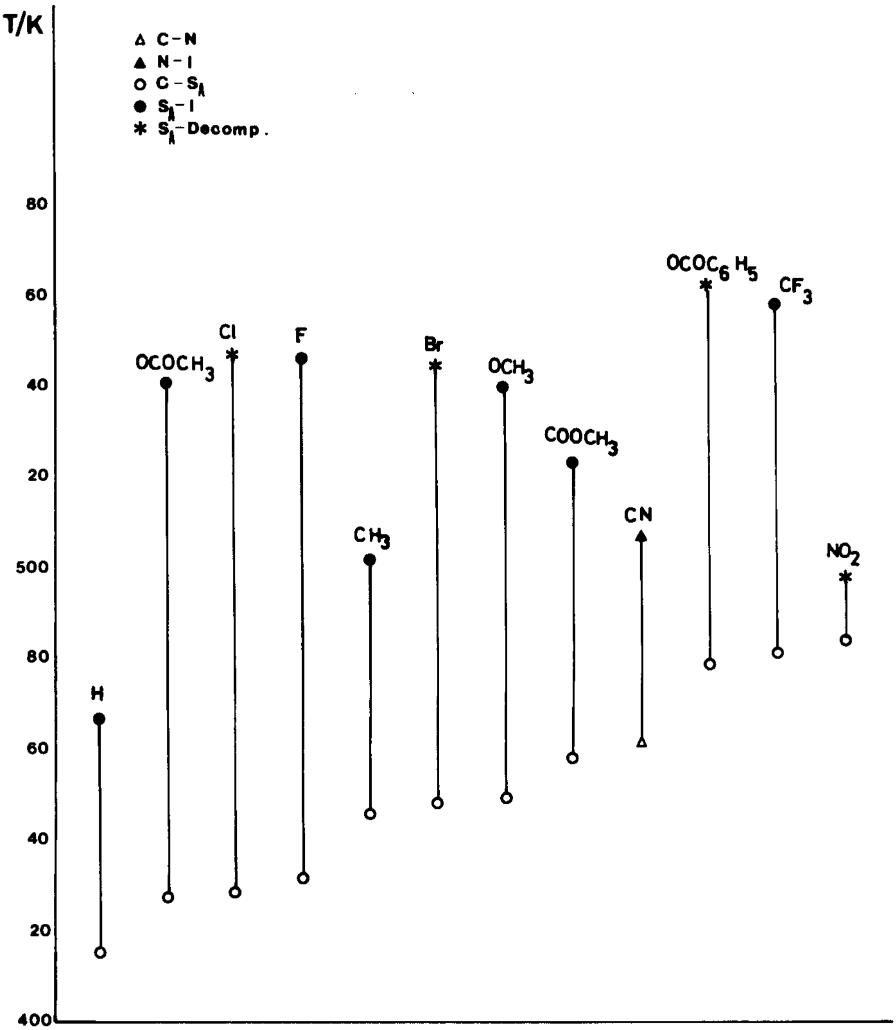


Figure 2. Transition temperatures of the chloro-bridged complexes $Pd_2(\mu\text{-}Cl)_2L_2$.

When the sample is allowed to remain at a fixed temperature between the two melting points for several minutes, the melt resolidifies and the whole sample melts at the higher melting point. On subsequent heating cycles this solid polymorphic form $C_3$ is not observed, and the sample melts at 415·1 K.

We assigned these complexes general dinuclear structures (see figure 3) similar to those assigned to the complexes studied in the previous paper [3], taking as our basis the analytical data of the complexes, their molecular weights together with their spectroscopic data [11]. The main structural difference between the complexes described results from the nature of the bridging *Y* group, and these differences explain the thermal behaviour of these two series of compounds. When the central bridge is an acetato group, it forces the two square planes of each palladium atom to form a very closed dihedral angle [3]. The whole molecule is non-planar with an open-book shape (see figure 4(*a*)). In the chloro-bridged complexes, however, the two square planes around each palladium atom should be in the same plane [3] (see figure 4(*b*)). The

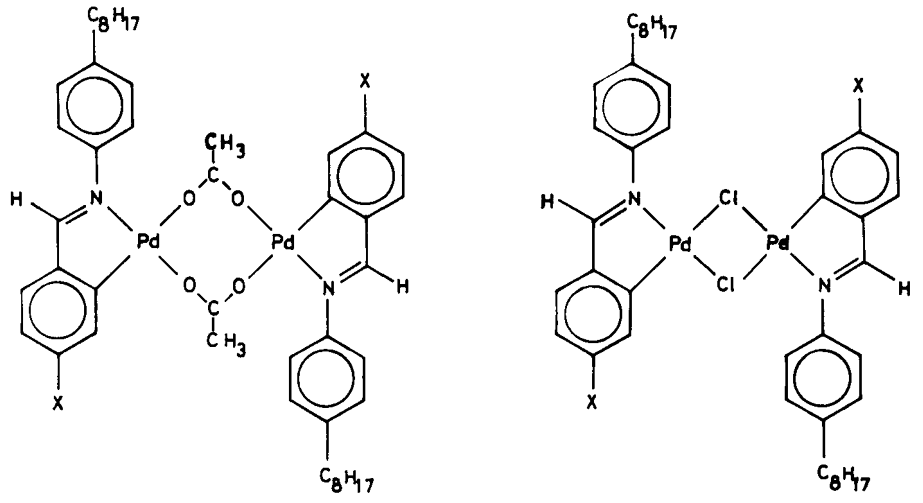


Figure 3. The structure of the two series of dinuclear derivatives of polar Schiff bases.

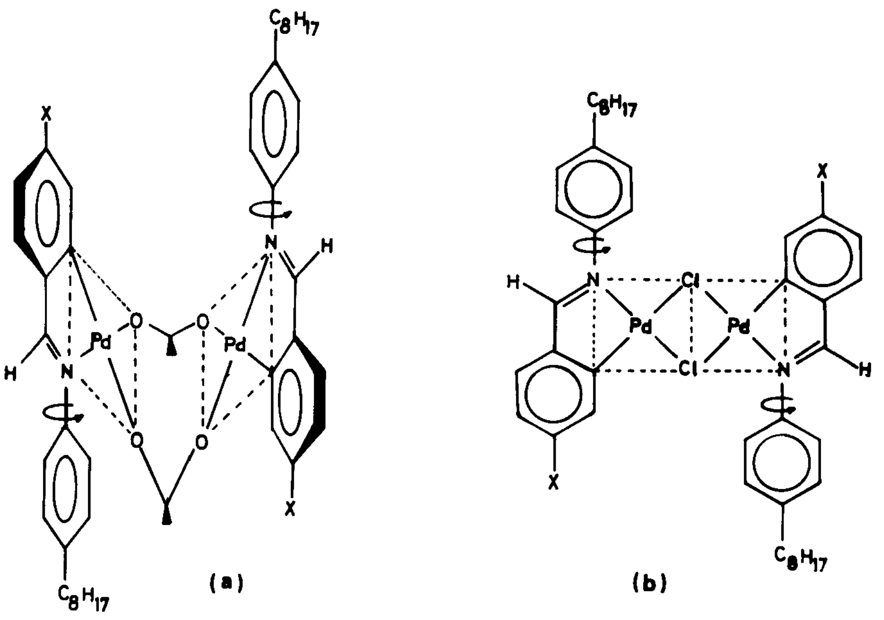


Figure 4. (*a*) The non-planar open book of the acetato-bridged complexes. (*b*) The planar structure of the chloro-bridged complexes.

interactions permitted by the planar structure between the central core of the molecules are sufficiently strong to prevent complete loss of molecular arrangement after melting. This, however, does not occur with the acetato-bridged complexes due to their different structure. When a strong dipole end group such as –CN or $-NO_2$ is present, these central core interactions seem to be made more difficult, possibly due to electronic repulsions. However, the group –CN stabilizes mesogenic molecular order of the nematic type, probably through interactions between the cyano polar group (–CN) and the imine bond (–C=N–) of the organic ligand.

## 4. Conclusion

Our study of the mesogenic properties of the ligands shows that in the Schiff bases studied, the mesophase arrangement (smectic A, smectic B or nematic) is determined by the polar end group. However, this is not normally the case with the chloro-bridged complexes where, with the exception of the compound with group $X$: –CN, all the compounds exhibit a smectic A mesophase. In this kind of compound, the central core of the molecule mainly determines the presence and type of mesogenic order; thus groups giving no mesophase in ligands ($X$: –H, –F and $-COOCH_3$) give mesomorphic properties in the complexes. The polar group which contributes to the anisotropy in the molecular polarizability, generally speaking, plays a secondary role, giving rise to the differences in the transition temperatures of the complexes.

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