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Doubly cyclopalladated pyridazines: chiral liquid crystals

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Abstract

The mono and dicyclopalladation of new mesogenic pyridazines and subsequent reaction with β-diketones yields some novel metallomesogens. The monometallated derivatives have a flat central core. In contrast, the dimetallated derivatives have a sterically induced twist in the molecule that renders them chiral. Smectic A phases are typically exhibited by both the derivatives with transition temperatures in the region of 100–300 °C.

Keywords: Cyclopalladated; Pyridazines; Mesogenic; Liquid crystal; Chiral

There is currently much interest in the synthesis of metal-containing liquid crystals due to the perceived advantages of combining the properties of liquid-crystal systems with those of transition metals. The area has been well reviewed recently [1–4], with excellent new work appearing constantly [5–12]. Cyclopalladated compounds have proved to be a particularly fertile area of research with many different examples from many different groups [13–29].

Previously, we have been studying a number of cyclopalladated Schiff's base compounds, using two very different co-ligands [30], variations on β-diketones [31], amino acids [32] and two metals within the central core [33]. Here we report our investigations into doubly cyclopalladated mesogens which are inherently chiral.

1. Synthesis

Four new series of mesogenic compounds were synthesised from 3,6-diphenylpyridazines (**1**): the monocyclometallated compounds **3** and **4** and the doubly cyclopalladated compounds **6** and **7** (Scheme 1). 3,6-Diphenylpyridazines (**1**) are conveniently prepared by the coupling of two equivalents of an aryl methyl ketone as has been described elsewhere [34].

Pyridazines (**1**) react cleanly with one equivalent of palladium acetate at 60 °C in acetic acid to yield a cyclopalladated species in high yield (Scheme 1). We presume this species is the dimer **2**, as an acetate-bridged dimer is a very common feature of similar palladium complexes [35]. We can then react this dimer with sodium acetylacetonate (acac) to yield the monomeric species **3**. Whilst we lack a single-crystal X-ray structure of **3**, all the data that we have (NMR spectroscopy, mass spectrometry and elemental analysis) are consistent with this formulation. The proton NMR spectrum of **3** is particularly useful, indicating the inequivalence of the two protons in the pyridazine ring, the presence of one metallated and one non-metallated phenyl ring and one acetylacetonate per pyridazine core. If we use two equivalents of palladium acetate (or indeed, react our monometallated species **2** with a second equivalent) and an extended reaction time, we can bring about a second cyclometallation to give a new species **5**. We have been unable to characterise the compound **5** in detail — solution NMR spectra are too broad to interpret — but we believe the compound to be doubly cyclopalladated. Whether **5** is polymeric with bridging acetate groups or, by analogy with other work [36,37], a simple dimer, is of little relevance here. Subsequent reaction of **5** with sodium acetylacetonate yields a well-characterised compound **6** with the formulation depicted in Scheme 1. In particular, the proton NMR spectrum of **6** is very informative: the aromatic region shows only four resonances of

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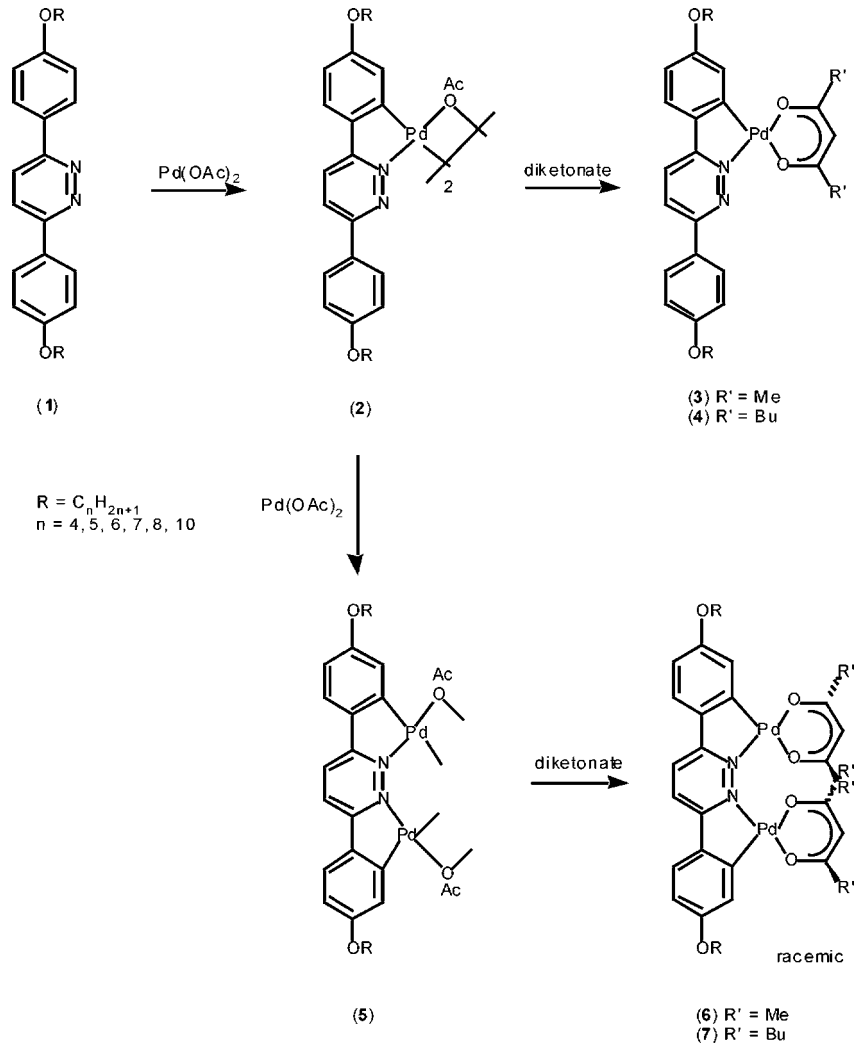
equal intensity (one singlet for the central pyridazine ring and three multiplets for the metallated ring, one doublet of 8.5 Hz, one doublet of 3 Hz and one double doublet of 8.5 and 3 Hz), there is a singlet for the central acetylacetonate proton of the same intensity as the aromatic resonances and the resonances for the methyl groups of the acetylacetonates are six times this intensity. Whilst we were unable to grow a crystal of **5** suitable for X-ray diffraction, all other data fit with this formulation.

Whilst we are confident that this is the correct formulation for **6**, it does raise the issue of the arrangement of the acetylacetonate groups. Simple modelling demonstrates the impossibility of achieving the preferred planar arrangement of the pyridazine core, both cyclometallated rings and both acetylacetonate groups — indeed this is one of the reasons we wanted to make these compounds. Hence, the helical twist on the structure of **6** suggested in Scheme 1. The practical effect of this twist is to reduce the symmetry of the compound, leaving a C_2 axis as the only symmetry element — hence the molecule must be chiral. It follows that, if these molecules are chiral, we must have a racemic mixture as no attempt was made to control any stereochemistry in the reaction. The solution state proton and carbon NMR spectra of **6** do not show any unusual features: neither the chemical shifts of the aromatic or acetylacetonate resonances are much different to those in the monocyclopalladated **3**. The only potentially significant feature of the solution NMR spectrum is the equivalence of the chemical shifts of the methyl groups of the acetylacetonate — both ends of the acetylacetonate resonate as singlets at 2.08 ppm in the proton NMR spectrum and at 27.4 ppm in the carbon NMR spectrum. This equivalence might at first suggest that the correct structure is one in which the palladiums are tetrahedral (with the acetylacetonate groups perpendicular to the pyridazine core) but this would require the palladiums to be paramagnetic, and the sharp NMR spectrum precludes this possibility.



Scheme 1.

Table 1
Mesogenic behaviour of 3,6-bis(4-alkoxyphenyl)pyridazines

n	Temperature/°C (ΔH/kJ mol^{-1})												
4	K	110 (0.11)	S_G	155 (6.97)	S_F	166 (1.43)	S_C	170 (11.9)	S_A	212 (0.11)	N	248 (1.3)	I
5	K	101 (24.7)	S_G	165 (12.1)	S_F	241 (6.43)	S_C	248 [a]	N	254 (3.64)	I		
6	K	87 (8.83)	K′	94 (15.4)	S_G	139 (0.17)	S_F	165 (0.91)	S_I	258 (11.2)	I		
7	K	112 (40.3)	K′	143 (10.3)	S_G	145 (0.04)	S_F	165 (1.47)	S_I	252 (13.1)	I		
8	K	109 (32.9)	K′	131 (10.1)	S_G	142 (0.10)	S_F	166 (1.32)	S_I	249 (13.3)	I		
10	K	113 (10.3)	K′	121 (10.0)	K″	129 (10.0)	S_G	163 (1.96)	S_F	238 (15.7)	I		

[a] Combined enthalpies.

Another interpretation of the solution NMR data is that the molecule is fluxional and the ends of the acetylacetonates are interchanging rapidly on the NMR timescale, but cooling the sample to −80 °C did not reveal any significant changes in the NMR spectrum. Thus we conclude that there is an accidental equivalence of the methyl groups in the NMR spectra and the structure is indeed the helically twisted one depicted in Scheme 1. Platinum derivatives of diphenyl pyridine with a similar sterically imposed helical twist have been isolated in good yields [38–42], indicating that our proposed structure is not unprecedented. In addition, our own work with doubly cycloplatinated pyridazines provides support for our formulation [43]. It is not obvious whether the enantiomers of our doubly cyclometallated acetylacetonate compound will be sufficiently configurationally stable to ever allow their separation.

In any event, the synthesis of the acetylacetonate derivatives **3** and **6** proceeded in good yield, and these complexes were purified by column chromatography before their mesogenic behaviour was investigated. In addition to the simple acetylacetonate derivatives, undecan-5,7-dione ('butyl acetylacetonate') derivatives of both the mono and dipalladated pyridazines, **4** and **7**, respectively, were also isolated. In addition to the expected reductions in transition temperatures the undecadione derivatives have the added benefit of greater chemical stability afforded by the butyl chains, 'protecting' the palladium, which helps to eliminate the problem of decomposition seen in the some of the acetylacetonate derivatives. The undecadione derivatives of the dipalladated compounds proved to be tricky to isolate in high yields. However, two analogues were successfully synthesised from the reaction of two equivalents of 5,7-undecadione and the dipalladated acetate-bridged compound **5**, in the presence of triethylamine, in tetrahydrofuran. The difficulties encountered in the syntheses are likely to be as a result of the steric interactions between what would be two neighbouring butyl chains in close proximity. Whilst it might be expected that a total of four butyl chains would enhance the thermal stability of these molecules, it might also be the case that the molecules would be destabilised due to steric affects. In any event, all characterisation was consistent with our proposed formulations. Altogether six different pyridazines were used giving a total of 20 new compounds.

2. Thermal properties

Whilst 3,6-bis-(4′-alkylphenyl)pyridazines have long been known to be mesomorphic [44], with mesophases in the 190–220 °C range, the 3,6-bis-(4′-alkyloxy phenyl)pyridazines we use here do not appear to have been studied before. All of the six homologues that we synthesised exhibited mesogenic phases in the 110–250 °C temperature range; their behaviour is detailed in Table 1 and summarised in Fig. 1. Phases were identified by their phase texture when viewed under the crossed polars of a polarising microscope; these textures are highly characteristic and can often be used to definitively assign the phase. Thus the nematic and smectic C phases exhibited schlieren textures, the nematic showing both 4 and 2 point brushes, the smectic C only 4 point brushes. The smectic F phase showed a schlieren-mosaic type texture on cooling from the smectic C. When both the smectic F and I phases were observed, the order allowed us to distinguish them. Transition temperatures were taken from the optical microscope and confirmed by the onset of transitions in the DSC.

Thus it can be seen that the longer terminal chain length analogues of **1**, C6–C10, show exclusively the ordered hexagonal mesophases (smectic I, smectic F and smectic G). This can be attributed to the rigid-planar structure of the mesogenic core (three directly connected para substituted aromatic rings). This allows highly efficient intermolecular hexagonal packing interactions between the molecules in the mesophase. As the chain length decreases (i.e. to five or four carbons) the more disordered mesophases (smectic C, smectic A and nematic phases) can be seen. This can be attributed to the decreased length to breadth ratio of the molecule.

The thermal behaviour of the monocyclopalladated acetylacetonate complexes **3** is listed in Table 2 and summarised in Fig. 2. As can be seen, all compounds

exhibited a smectic A phase. This smectic A phase was identified by its phase texture, which appears as a focal-conic fan texture; such a texture is highly characteristic and can be used to definitively assign the phase. Note that apart from the smectic B phase between the crystal and smectic A phase exhibited by the shortest chained homologue, no liquid crystal phase types other than the smectic A were observed for these derivatives. A general trend of decreasing clearing point temperatures with an odd-even effect was seen as the chain

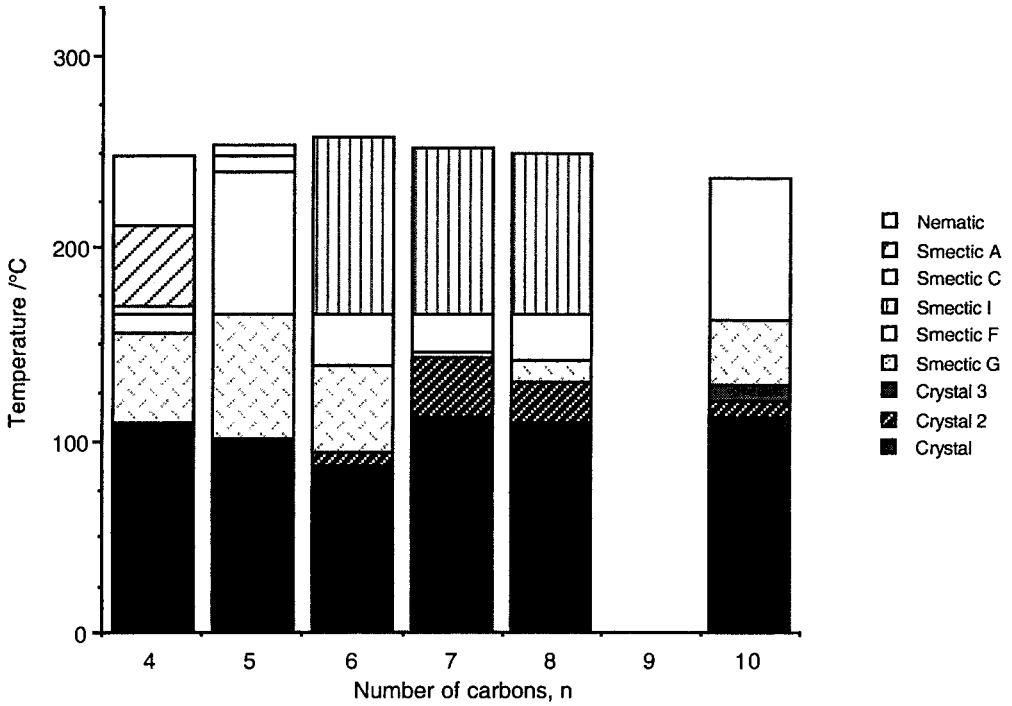


Fig. 1. Phase behaviour, compounds **1**.

Table 2
Mesogenic behaviour of compounds **3**, **4**, **6** and **7**

Compound	*n*	Transition temperature/°C (ΔH/kJ mol^{-1})						
3	4	K	156 (8.48)	S_B	183 (15.9)	S_A	276 [a] (0.58)	I
	5	K	182 (10.1)	S_A	310 [a]	I		
	6	K	196 (21.8)	S_A	280 [a] (0.57)	I		
	7	K	196 (22.9)	S_A	290 [a](0.95)	I		
	8	K	162 (23.3)	S_A	264 [a] (1.51)	I		
	10	K	184 (22.7)	S_A	281 [a] (1.77)	I		
4	4	K	154 (16.9)	S_A	184 [b]	I		
	5	K	154 (10.2)	S_A	180 (1.9)	I		
	6	K	112 (10.2)	S_A	190 (0.14)	I		
	7	K	119 (19.2)	S_A	185 (0.07)	I		
	8	K	104 (17.6)	S_A	186 (1.4)	I		
	10	K	90 (43.1)	S_A	180 (1.2)	I		
6	4	Decomposition below 260						
	5	K	244 [a]	S_A				
	6	K	236 [a]	S_A				
	7	K	244 [a]	S_A				
	8	K	147 (23.6)	S_A	250 [a]	I		
	10	K	169 (29.1)	S_A	210 [a]	I		
7	5	K	128	I				
	6	K	123	I				

[a] With decomposition.
[b] Combined enthalpies.

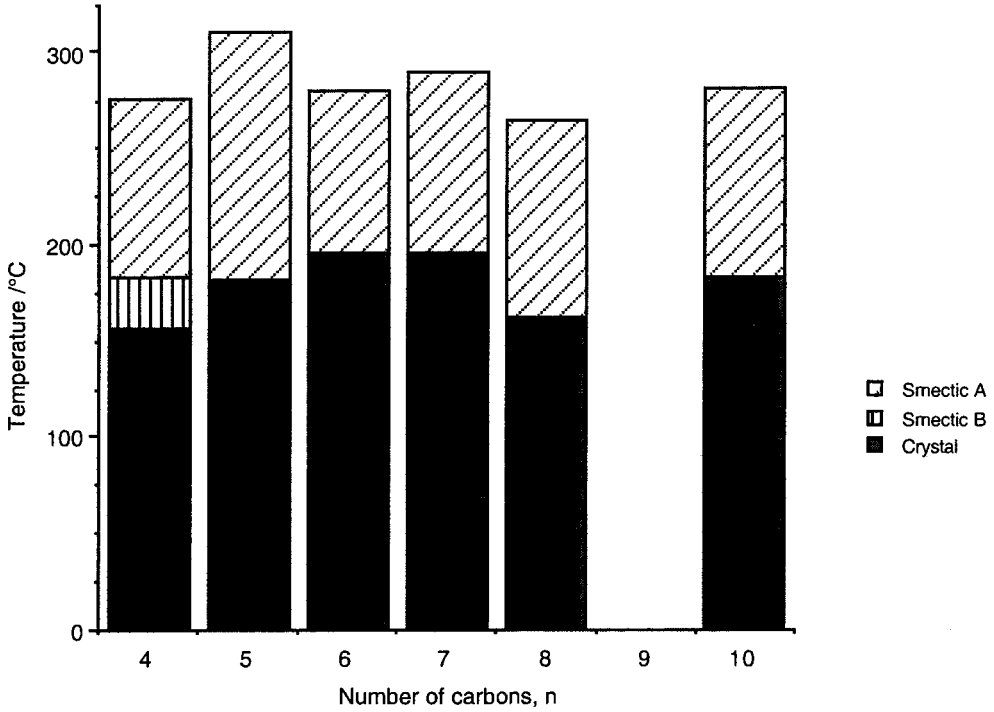


Fig. 2. Phase behaviour, compounds **3**.

length increased, but in all cases, there was a problem of decomposition in the isotropic liquid due to the high temperatures involved.

When one compares the pyridazines (**1**) with the monopalladium acetylacetonate compounds **3** it is immediately apparent that the melting points have been increased by some 50 K with the presence of the Pd(acac) moiety. Whilst one might expect that the presence of the Pd(acac) moiety would increase the width of the calamitic mesogen and consequently reduce its rod-like nature and ability to pack, resulting in lower melting points, one might also expect the increased mass to result in an increased melting temperature. In a previous case of Pd(acac) derivatives of some Schiff's base derived ligands we observed an effective cancellation of these factors, resulting in an essentially unchanged melting point [30]. In parallel to the increase in the melting points observed for compounds **3**, the clearing points have increased by some 30–40 K, resulting in these monopalladated compounds exhibiting a slightly smaller mesogenic range to their parent pyridazines. The absence of the more ordered smectic I, F and G phases that the pyridazines show is to be expected as the palladium acetylacetonate unit would be expected to break up the lateral forces required for such phases.

In an attempt to lower the transition temperatures, and overcome the problem of decomposition, monopalladated acetate-bridged dimers **2** were reacted with 5,7-undecadione, in place of acetylacetone, to give compounds **4**. The lowering of the transition temperatures is expected because the butyl chains of the diketone will disrupt the molecule's ability to pack in orderly mesophases [31]. Thermal behaviour was examined using hot-stage polarising microscopy and DSC. Full data are listed in Table 3 and summarised in Fig. 3.

As expected the longer chain β-diketones caused a lowering in the melting temperatures of the materials causing them to decrease by nearly 100 K in some cases, when compared to the acetylacetonate derivatives. A slightly larger lowering of the smectic A to isotropic phase transition can also be seen, resulting in a reduced mesogenic range for compounds **4** compared with compounds **3**. This effect can be attributed to the fact that the longer chains further disrupt the ability of the molecules to pack in an orderly fashion. In addition, there is also the added benefit of greater chemical stability afforded by the butyl chains, 'protecting' the palladium, this helps to eliminate the problem of decomposition seen in the acetylacetonate derivatives. Thus, by comparison with their simple acetylacetonate analogues, the monopalladated undecadione derivatives are chemically more robust and exhibit their mesophases at more accessible temperatures, albeit with a slightly reduced mesogenic range.

A series of *cis*-dicyclopalladated acetylacetonate analogues **6** were synthesised and their thermal behaviour examined. Full data are summarised in Table 2. All members of the series did show some mesogenic character, exclusively exhibiting a smectic A phase. No clearing point was observed for the C5, C6 and C7 analogues due to decomposition.

Table 3
Elemental analysis data for compounds **1**, **3**, **4**, **6** and **7**

Compound	*n*	C (%) Found	Expected	H (%) Found	Expected	N (%) Found	Expected
1	4	77.0	76.6	7.4	7.5	7.1	7.4
	5	76.9	77.2	8.0	8.0	6.7	6.9
	6	77.6	77.7	8.3	8.4	6.5	6.5
	7	78.0	78.2	8.7	8.8	6.2	6.1
	8	78.3	78.7	8.9	9.1	5.7	5.7
	10	79.3	79.4	9.6	9.6	5.3	5.1
3	4	60.0	60.0	5.7	5.9	4.4	4.8
	5	62.2	61.1	6.6	6.3	4.4	4.6
	6	61.9	62.2	6.7	6.6	4.1	4.4
	7	63.5	63.2	7.1	7.0	4.2	4.2
	8	64.5	64.1	7.4	7.3	3.8	4.0
	10	65.6	65.7	7.8	7.8	3.7	3.7
4	4	63.3	63.2	7.0	6.9	4.0	4.2
	5	63.5	64.1	7.3	7.2	3.9	4.1
	6	65.0	65.0	7.4	7.5	3.5	3.9
	7	64.8	65.7	7.8	7.8	3.6	3.7
	8	65.6	66.4	8.1	8.0	3.5	3.6
	10	67.1	67.7	8.4	8.5	3.2	3.4
6	4	49.6	51.9	5.2	5.4	3.4	3.6
	5	48.6	53.1	5.1	5.4	3.3	3.4
	6	46.4	54.2	5.0	5.7	3.0	3.3
	7	50.4	55.2	5.4	6.0	3.1	3.2
	8	47.6	56.2	5.4	6.3	2.8	3.1
	10	56.9	57.9	6.7	6.8	2.8	2.9
7	5	56.8	58.7	6.5	7.0	2.1	2.8
	6	56.0	59.4	7.0	7.2	2.5	2.8

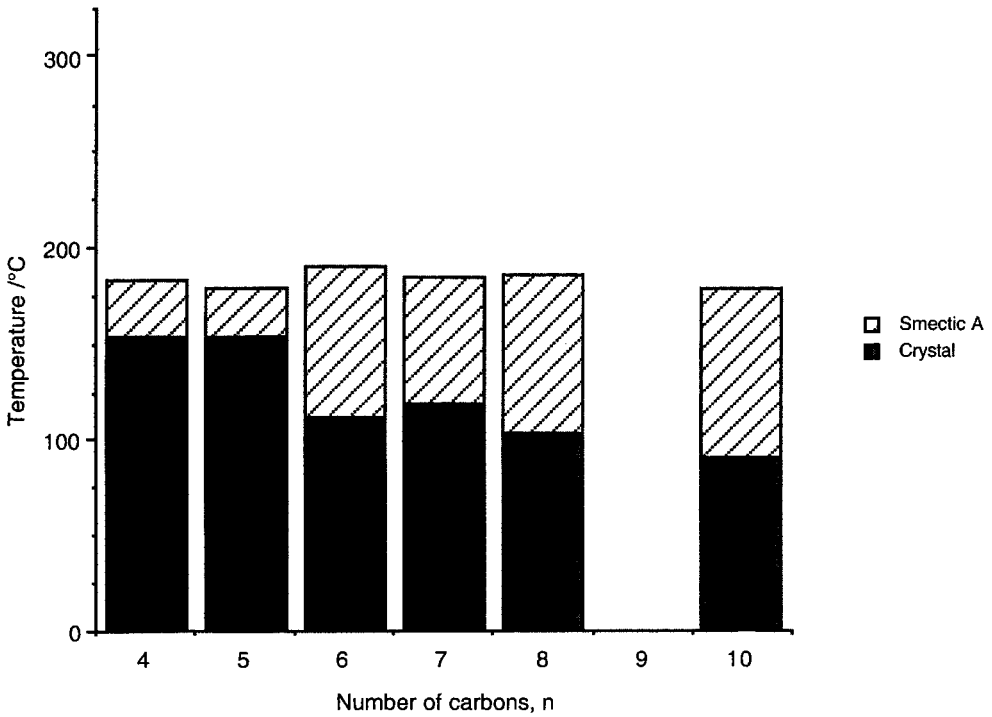


Fig. 3. Phase behaviour, compounds **4**.

On heating extensive decomposition, due to the low chemical stability of the molecules, was seen in all the examples. The temperatures at which these dipalladated molecules **6** exhibit their mesophases is always considerably higher than that exhibited by their monopalladated analogues **3**. Presumably the extra mass of the second palladium acetylacetonate unit within the molecules results in a greater increase in the transition temperatures than can be compensated for by the additional disruption that this group makes to the solid-state packing (and hence reduction in the transition temperatures) [45]. The lack of any long-lived mesogenic behaviour in the shorter chain lengths can be attributed to the reduction in length to breadth ratio when the second acetylacetonate group is added. In addition, the symmetrical nature of these molecules is of relevance, as a symmetrical arrangement of this type is often responsible for higher melting points [46,47]. The observation of only a smectic A phase is unfortunate as there is no distinction between the chiral and non-chiral variants.

As with the monopalladated derivatives a different β-diketone, 5,7-undecadione was used in place of the acetylacetone in an attempt to induce more chemical stability in the molecule so that mesophases could be observed without decomposition. Attempts at synthesising this series of compounds have been somewhat unreliable. Two analogues have, however, been successfully synthesised, from the reaction of two equivalents of 5,7-undecadione and the dipalladated acetate-bridged ligand **5**, in the presence of triethylamine, in tetrahydrofuran, at room temperature, over 4 h. The difficulties encountered in the syntheses are likely to be as a result of the steric interactions between what would be two neighbouring butyl chains in close proximity. As was seen in the monopalladated examples, it might be expected that there would be enhanced thermal stability of these molecules, as a result of the protecting butyl chains. In this case, however, the molecules might be destabilised due to steric affects.

The $n = 5$ and 6 derivatives that have been synthesised did not show any mesogenic behaviour with both melting directly into the isotropic liquid below 130 °C, presumably the extra four lateral alkyl chains increase the width of the molecules by too great an extent for any mesophases to exist.

3. Conclusions

Pyridazines have proved to be versatile compounds: in there own right they exhibit rich mesogenic behaviour, and they can be readily derivatised. Thus we have investigated both singly and doubly cyclopalladated derivatives. These derivatives also exhibit mesogenic behaviour with both smectic A and B phases being observed; we have the ability to tune transition temperatures by varying ligands.

4. Experimental

4.1. General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained in either a Bruker Avance 300, 400 or 500 in $CDCl_3$ and are referenced to external TMS, assignments being made with the use of decoupling, nOe and the DEPT and COSY pulse sequences. Thermal analyses were performed in an Olympus BH2 microscope equipped with a Linkam HFS 91 heating stage and a TMS90 controller, at a heating rate of 10 K min^{-1}, and a Perkin–Elmer Pyris 1 DSC. All elemental analyses were performed by Warwick Analytical Service.

4.2. Preparation of 3,6-bis(4′-n-alkyloxphenyl)pyridazines (*1*)

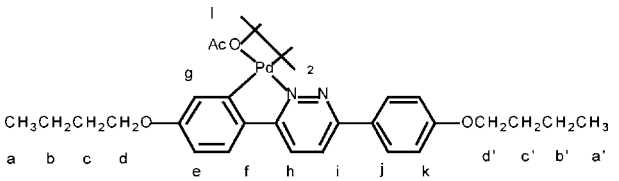
Six homologues ($n = 4$, 5, 6, 7, 8, and 10) were prepared in good yields (50–70%) using a literature procedure [34]. The mesogenic behaviour of all homologues is summarised in Fig. 1, and detailed in Table 1. Elemental analyses are detailed in Table 3.

4.3. Preparation of dipalladium(μ-acetato)-3,6-bis(4′-butyloxyphenyl)pyridazine (*2*)

The butyloxy derivative is described in detail, all other homologues were prepared similarly.

Palladium acetate (0.059 g, 2.63×10^{-4} mol) was added to a solution of 3,6-bis(4′butyloxyphenyl)-pyridazine (0.1 g, 2.63×10^{-4} mol) in AcOH (25 cm^3) and heated (60 °C, 48 h). The solvent was removed to yield a yellow solid (0.143 g, 1.31×10^{-4} mol, yield assumed to be 100%).

4.3.1. NMR data for compound *2*



δ_H ($CDCl_3$): 7.95 (2H, AA′XX′, $J = 7.5$ Hz, H_j), 7.45 (1H, d, $^3J = 8.5$ Hz, $H_{h/i}$), 7.05 (1H, d, $^3J = 8.5$ Hz, $H_{h/i}$), 7.00 (2H, AA′XX′, $J = 7.5$ Hz, H_k), 6.75 (1H, d, $^3J = 8.5$ Hz, H_f), 6.30 (1H, d, $^4J = 2.5$ Hz, H_g), 6.25 (1H, dd, $^3J = 8.5$ Hz, $^4J = 2.5$ Hz, H_e), 4.00 (4H, t,

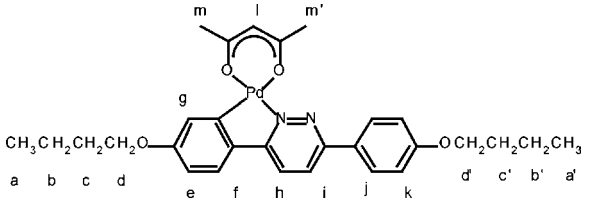
$H_{d/d'}$), 2.35 (3H, s, H_l), 1.80 (4H, m, $H_{c/c'}$), 1.45 (4H, m, $H_{b/b'}$), 0.95 (6H, m, $H_{a/a'}$).

4.4. Preparation of palladium(acac)-[3,6-bis(4-butyloxyphenyl)pyridazine] (3)

The butyloxy derivative is described in detail, all other homologues were prepared similarly.

Sodium acetylacetonate (0.036 g, 2.63×10^{-4} mol) was added to a solution of dipalladium(μ-acetato)-3,6-bis(4′-butyloxyphenyl)pyridazine (1.31×10^{-4} mol) in acetone (30 cm^3). The solution was stirred at room temperature (r.t.) for 18 h and the solvent removed to yield a yellow solid that was purified on a silica column using a 90:10, $CHCl_3$–MeOH elutant. The solvent was removed to yield a crystalline yellow solid (0.11 g, 1.92×10^{-4} mol, 73% yield).

4.4.1. NMR data for compound 3



δ_H ($CDCl_3$): 8.05 (2H, AA′XX′, $J = 7.5$ Hz, H_j), 7.90 (1H, d, $^3J = 9$ Hz, $H_{h/i}$), 7.65 (1H, d, $^3J = 9$ Hz, $H_{h/i}$), 7.35 (1H, d, $^3J = 8.5$ Hz, H_f), 7.25 (1H, d, $^4J = 2.5$ Hz, H_g), 6.95 (2H, AA′XX′, $J = 7.5$ Hz, H_k), 6.65 (1H, dd, $^3J = 8.5$ Hz, $^4J = 2.5$ Hz, H_e), 5.45 (1H, s, H_l), 4.10 (2H, t, $^3J = 6$ Hz, $H_{d/d'}$), 4.00 (2H, t, $^3J = 6$ Hz, $H_{d/d'}$), 2.15 (3H, s, $H_{m/m'}$), 2.10 (3H, s, $H_{m/m'}$), 1.75 (4H, m, $H_{c/c'}$), 1.50 (8H, m, $H_{b/b'}$), 0.95 (6H, m, $H_{a/a'}$). FABMS (NBA); m/z: 581 (largest, $[M^+]$), 482 ($[M^+] - acac$).

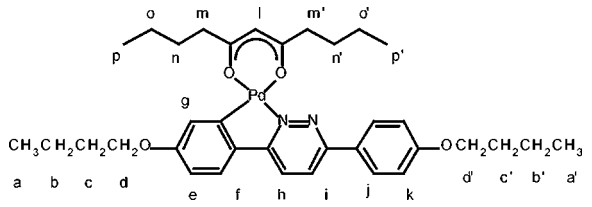
The mesogenic behaviour of all homologues is summarised in Fig. 2, and detailed in Table 2. Elemental analyses are detailed in Table 3.

4.5. Preparation of palladium(5,7-undecadione)-[3,6-bis(4-hexyloxyphenyl)pyridazine] (4)

The hexyloxy derivative is described in detail, all other homologues were prepared similarly.

5,7-Undecadione (0.043 g, 2.31×10^{-4} mol) and Et_3N (0.023 g, 2.31×10^{-4} mol) were added to a solution of dipalladium(μ-acetato)-3,6-bis(4-hexyloxyphenyl)pyridazine ($1{,}15 \times 10^{-4}$ mol) in THF (60 ml). The reaction mixture was stirred overnight at r.t. The solvent was removed to yield a yellow solid which was purified by chromatography on silica, eluting with $CHCl_3$–MeOH (90:10). The solvent was removed under reduced pressure to yield a bright yellow solid (0.08 g, 1.15×10^{-4} mol, 49% yield).

4.5.1. NMR data for compound 4



δ_H ($CDCl_3$): 8.00 (2H, AA′XX′, $J = 7.5$ Hz, H_j), 7.85 (1H, d, $^3J = 8.5$ Hz, $H_{h/i}$), 7.65 (1H, d, $^3J = 8.5$ Hz, $H_{h/i}$), 7.28 (1H, d, $^3J = 7.6$ Hz, H_f), 7.25 (1H, d, $^4J = 2.5$ Hz, H_g), 6.90 (2H, AA′XX′, $J = 7.5$ Hz, H_k), 6.65 (1H, dd, $^3J = 7.6$ Hz, $^4J = 2.5$ Hz, H_e), 5.35 (1H, s, H_l), 4.05 (2H, t, $^3J = 6.9$ Hz, $H_{d/d'}$), 3.95 (2H, t, $^3J = 6.9$ Hz, $H_{d/d'}$), 2.30 (4H, m, $H_{c/c'}$), 1.70 (8H, m, $H_{m/m'}$), 1.40 (12H, m, $H_{n/n'/o/o'/b/b'}$), 0.90 (12H, m, $H_{a/a',y/y'}$). FABMS (NBA); m/z: 665 $[M^+]$, 482 (largest, $[M^+]$ − undecandione).

The mesogenic behaviour of all homologues is summarised in Fig. 2, and detailed in Table 2. Elemental analyses are detailed in Table 3.

4.6. Preparation of bis-palladium-bis(μ-acetato)-3,6-bis(4′-butyloxyphenyl)pyridazine (5)

The butyloxy derivative is described in detail, all other homologues were prepared similarly.

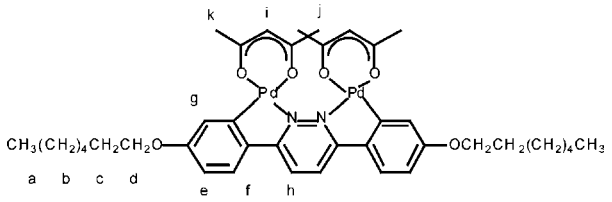
Palladium acetate (0.24 g, 1.06×10^{-3}) was added to a solution of 3,6-bis(4-pentyloxyphenyl)pyridazine (0.20 g, 5.32×10^{-4} mol) in MeOH (100 ml). The reaction mixture was heated to 60 °C and stirred for 2 days to yield a dark red–orange solution. The solvent was removed under reduced pressure and the solid dissolved in $CHCl_3$ and filtered through celite to remove traces of palladium black. The $CHCl_3$ was removed under reduced pressure to yield a dark red solid. NMR too broad to interpret.

4.7. Preparation of [bis-palladium-bis(acetylacetonate)-{3,6-bis(4-heptyloxyphenyl)pyridazine}] (6)

The heptyloxy derivative is described in detail, all other homologues were prepared similarly.

Sodium acetylacetonate (0.052 g, 4.35×10^{-4} mol) was added to a solution of bis-palladium-bis(μ-acetato)-3,6-bis(4′-heptyloxyphenyl)pyridazine (0.100 g, 1.18×10^{-4} mol) in THF (125 ml). The solution was stirred at r.t. for 4.5 h and the solvent removed. The resulting yellow–orange product was washed with hexane (10 ml × 2) and Et_2O (10 ml × 2) to yield a yellow solid which was dried under vacuum (0.090 g, 1.04×10^{-4} mol, 87%).

4.7.1. NMR data for compound ***6***



δ_H ($CDCl_3$): 7.80 (2H, s, H_h), 7.25 (2H, d, $^3J = 8.5$ Hz, H_f), 7.10 (2H, d, $^4J = 3$ Hz, H_g), 6.65 (2H, dd, $^3J = 8.5$ Hz, $^4J = 3$ Hz, H_e), 5.35 (2H, s, H_i), 4.00 (4H, t, $^3J = 7.5$ Hz, H_d), 2.08 (12H, s, $H_{j/k}$), 1.80 (4H, m, H_c), 1.30 (16H, m, H_b), 0.95 (6H, t, H_a). FABMS (NBA); m/z: 771 (largest, $[M^+] -$ acac), 665 ($[M^+] -$ Pd acac).

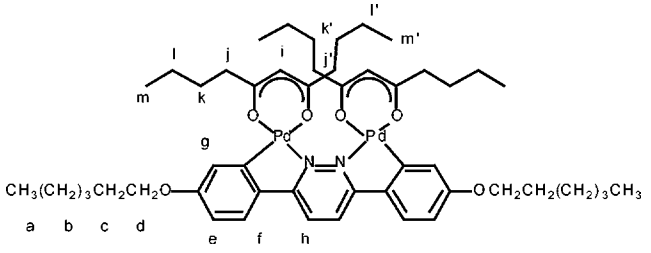
The mesogenic behaviour of all homologues is summarised in Fig. 3, and detailed in Table 2. Elemental analyses are detailed in Table 3.

4.8. Preparation of [bis-palladium-bis(5,7-undecadione)-{3,6-bis(4-hexyloxyphenyl)pyridazine}] ***(12)***

The hexyloxy derivative is described in detail, all other homologues were prepared similarly.

5,7-Undecadione (0.084 g, 4.58×10^{-4} mol {excess}), and Et_3N (0.046 g, 4.58×10^{-4} mol) were added to a stirred solution of bis-palladium-bis(μ-acetato)-3,6-bis(4′-hexyloxyphenyl)pyridazine (0.10 g, 1.14×10^{-4} mol) in THF (100 ml). The reaction mixture was left overnight at r.t. and the solvent removed to yield a sticky-yellow product. This was dissolved in $CHCl_3$ and washed with water. The $CHCl_3$ solution was dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure, to yield a yellow solid. The product was washed with hexane and Et_2O (0.021 g, 2.03×10^{-5} mol, 18%).

4.8.1. NMR data for compound ***12***



δ_H ($CDCl_3$): 7.70 (2H, s, H_h), 7.15 (2H, d, $^3J = 8$ Hz, H_f), 7.08 (2H, d, $^4J = 2$ Hz, H_g), 6.57 (2H, dd, $^3J = 8$ Hz, $^4J = 2$ Hz, H_e), 5.1 (2H, s, H_i), 3.98 (4H, t, H_d), 2.15 (4H, m, H_c), 1.70 (8H, m, $H_{j,j'}$), 1.25 (28H, m, $H_{b,k,k',l,l'}$), 0.90 (18H, m, $H_{a,m,m'}$). FABMS (NBA); m/z: 855 (largest, $[M^+] -$ undecandione), 749 ($[M^+] -$ Pd undecandione).

The mesogenic behaviour of all homologues is detailed in Table 2. Elemental analyses are detailed in Table 3.

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