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Chiral cyclopalladated liquid crystals from amino acids

Daniel J. Saccomando, Catherine Black, Gareth W.V. Cave, Donocadh P. Lydon, Jonathan P. Rourke *

Department of Chemistry, Warwick University, Coventry CV4 7AL, UK

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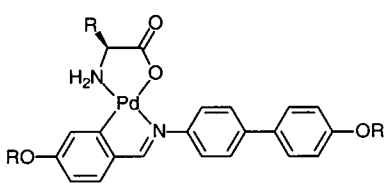
Abstract

The cyclopalladation of mesogenic Schiff bases and subsequent reaction with natural L-amino acids yields a novel series of metallomesogens. The transition temperatures of the complexes are uniformly higher that those of the free ligands, with smectic A phases being exhibited.



Keywords: Liquid crystals; Amino acids; Mesogenic; Schiff bases; Palladium

1. Introduction

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 [1–6], with excellent new work appearing constantly [7–15]. Cyclopalladated compounds have proved to be a particularly fertile area of research, with many different examples from many different groups [9,16–31].

Previously, we have been studying a number of cyclopalladated Schiff base compounds using two very different co-ligands [32], variations on β-diketones [33], and two metals within the central core [34]. Here we report our investigations into chiral cyclopalladated mesogens using a number of different natural amino acids as co-ligands.

2. Synthesis

The synthesis of the new compounds described here is summarised in Scheme 1. The synthesis of the 4-alkyloxy-*N*-(4′-alkyloxybiphenyl)benzylidene ligands (**1**) via a simple condensation of the appropriate aldehyde and aniline proceeded in high yield and has been described elsewhere [32]. The cyclopalladation step to give the intermediate **2** was essentially quantitative, and **2** was used without further purification. The synthesis of the amino acid derivatives from **2** proceeded in good yield, and these complexes were purified by column chromatography. The reaction of compounds analogous to **2** with amino acids has been shown to proceed in a regiospecific manner, yielding only the compound with nitrogen *trans* to nitrogen [35,36]. Four different amino acids were used: alanine, valine, leucine and isoleucine, giving the cyclopalladated complexes **3**, **4**, **5** and **6**, respectively. All these homologues were analysed by ^{1}H-NMR, the characteristic features of the spectra being a singlet peak for the imine, two broad peaks for the amino hydrogens and a multiplet for the amino acid alpha hydrogen. The compounds gave good elemental

* Corresponding author. Tel.: +44-2476-523263; fax: +44-2476-524112.

E-mail address: j.rourke@warwick.ac.uk (J.P. Rourke)

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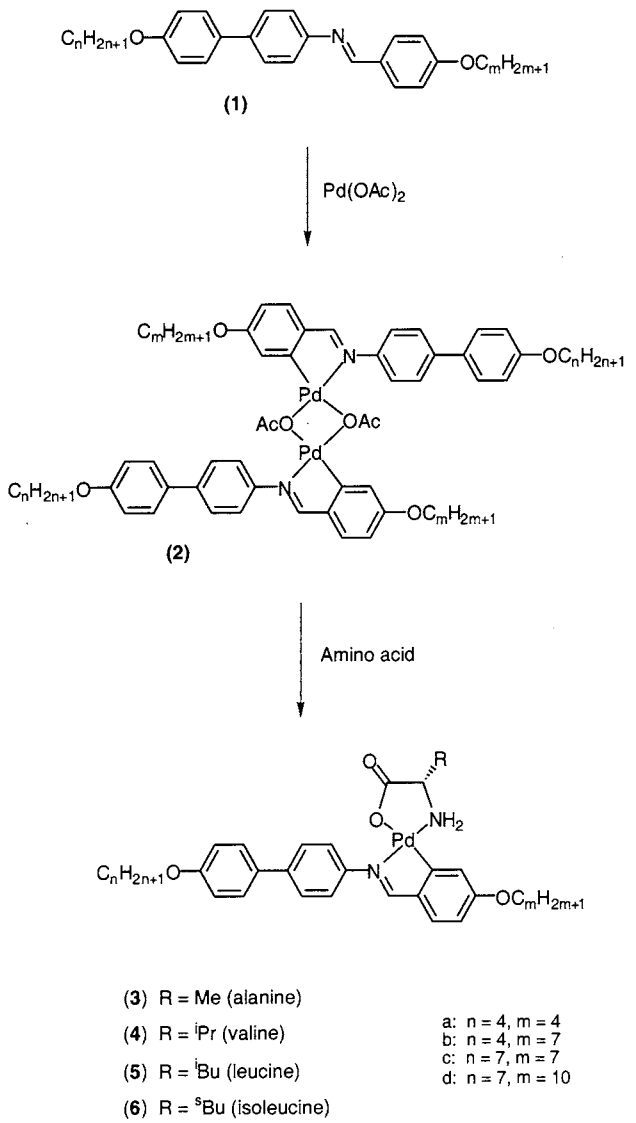


Scheme 1.

analyses (Table 2). Altogether four different Schiff bases and four different amino acids were used giving a total of 16 new compounds.

3. Thermal properties

The thermal behaviour of the ligand **1** has been reported before [32], and is summarised in Fig. 1.

The thermal behaviour of the amino acid complex is listed in Table 1 and summarised in Fig. 2. As can be seen, all compounds (except **3a**) 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. Transition temperatures were taken from the optical microscope and confirmed by the onset of transitions in the DSC (where appropriate). Given the extensive decomposition that accompanied many of the transitions, it was felt that no meaningful measure of enthalpies could be taken from the DSC data. Note that no liquid-crystal phase types other than the smectic A were observed. Compound **3a**, the most compact of those we studied, melted directly into the isotropic liquid.

Fig. 2 shows the thermal behaviour with the compounds grouped according to the type of amino acid used. Given the lack of thermal stability of the compound once in the mesophase and the inability to determine a clearing point accurately, Fig. 2 only shows the melting points of the new complexes. The range of the mesophases is thus indeterminate. However, since we know that all of the compounds decompose at around 250°C and that some of them have been in the mesophase for 50 K at that point, we can assume that a healthy mesogenic range would have been exhibited by most of the compounds. For some of the compounds (**3a**, **3c**, **4a**, **5a** and **6a**) an isotropic liquid is seen around at 240–260°C and we can assume that the clearing point of the compounds that decomposed before clearing would probably not have been much different.

When one compares the ligands **1** with compounds **3**–**6**, it is immediately apparent that the melting points have been increased by some 50 K with the presence of the Pd (amino acid) moiety. While one might expect that the presence of the Pd (amino acid) 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 the case of the Pd(acac) derivatives of **1**, we observed an effective cancellation of these factors, resulting in an essentially unchanged melting point [32]. While the acetyl acetonate (acac) ligands are not exceptionally different in size from the amino acid ligands, it is clear that the amino acid groups somehow manage to further stabilise intermolecular interactions within the crystal lattice. This could be explained by intermolecular hydrogen bonding between the NH_2 and the carboxyl groups within the amino acid groups. This hydrogen bonding would cause greater attractions between the individual molecules, and hence cause an increase in the melting points. Although the acac complexes also contain oxygen and hydrogen, the oxygens are unable to hydrogen bond as they are involved in a pseudo aromatic complex with the palladium, and there are no polarised hydrogens.

The addition of the Pd (amino acid) moiety also results in the absence of the more ordered (and tilted) smectic C, F and G phases that the ligands exhibit, with only the less ordered smectic A phase being exhibited. This is not unexpected as the Pd (amino acid) moiety will disrupt the lateral interactions that are necessary

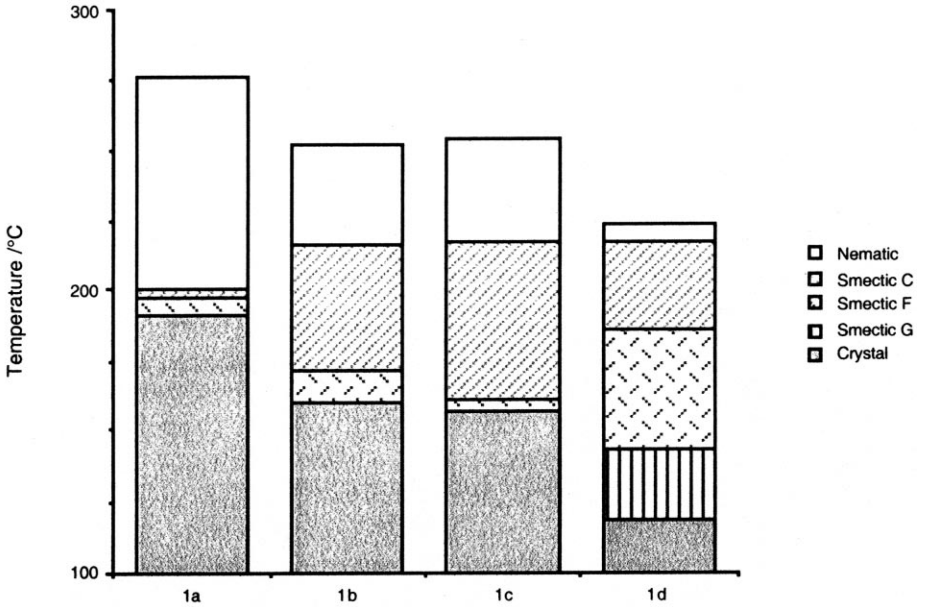


Fig. 1. Phase behaviour, compounds **1**.

for the more ordered phases and intrude upon a tilted arrangement. The observation of only a smectic A phase is unfortunate as there is no distinction between the chiral and non-chiral variants. Unfortunately, all the amino acid complexes **3**, **4**, **5** and **6** decompose around 250°C and none of them was seen to enter the isotropic liquid without decomposition, and a good number of them decomposed before they showed any sign of clearing. Hence, Fig. 2 only shows the melting points — a rough estimate can be made of the temperature they enter another phase or clear, but it would be inappropriate to include it in the Figure. This degree of thermal stability is consistent with other 16-electron square-planar palladium complexes, where decomposition occurs at around 250°C [34]. With the 18-electron trigonal bipyramidal cyclopentadiene complexes of palladium decomposition at around 180°C is more usual [32].

When one looks at the phase behaviour of the complexes grouped by amino acid (i.e. the effect of the Schiff base unit) in Fig. 2, it is immediately apparent that the second and fourth compounds (**b** and **d**) in each grouping have significantly lower melting points than the other two (**a** and **c**). Compounds **a** and **c** have equal length alkyloxy chains (four and seven carbons, respectively) on their central core, giving rise to a symmetrical arrangement. A symmetrical arrangement of this type is often responsible for higher melting points [37,38]. Within each grouping this effect is greatest for the alanine compounds **3**, and appears to diminish as one moves to the valine, leucine and isoleucine derivatives. The diminishing of this effect might well be expected as one would expect the larger amino acids derivatives to be proportionately less influenced.

When one looks at the phase behaviour of the complexes grouped by Schiff base (i.e. the effect of the amino acid moiety), the trends are less obvious. We had expected the melting points to show a dramatic drop as one moved from alanine through to isoleucine, paralleling the effects we observed when acac derivatives with alkyl chains were used [33]. However, such an effect is not clearly seen here, although the two symmetrical compounds (**a** and **c**) do show a lowering of melting point from alanine to valine to leucine with a slight increase to isoleucine.

When comparing the thermal properties of compounds **3**–**6** with that of their acac derivatives, it can be

Table 1
Mesogenic behaviour of compounds **1**, **3** and **5**

Compound	*Trans*	*T* (°C)	*Trans*	*T* (°C)
3a	Cry-I	256 [a]		
3b	Cry-S_A	216	S_A-dec	250 [a]
3c	Cry-S_A	253 [b]		
3d	Cry-S_A	201	S_A-dec	250 [a]
4a	Cry-S_A	244 [b]		
4b	Cry-S_A	232	S_A-dec	250 [a]
4c	Cry-S_A	242	S_A-dec	250 [a]
4d	Cry-S_A	220	S_A-dec	250 [a]
5a	Cry-S_A	231 [b]		
5b	Cry-S_A	216	S_A-dec	250 [a]
5c	Cry-S_A	231	S_A-dec	250 [a]
5d	Cry-S_A	217	S_A-dec	250 [a]
6a	Cry-S_A	241 [b]		
6b	Cry-S_A	234	S_A-dec	250 [a]
6c	Cry-S_A	236	S_A-dec	250 [a]
6d	Cry-S_A	223	S_A-dec	250 [a]

[a] With decomposition.
[b] Phase change accompanied by decomposition within 5 K.

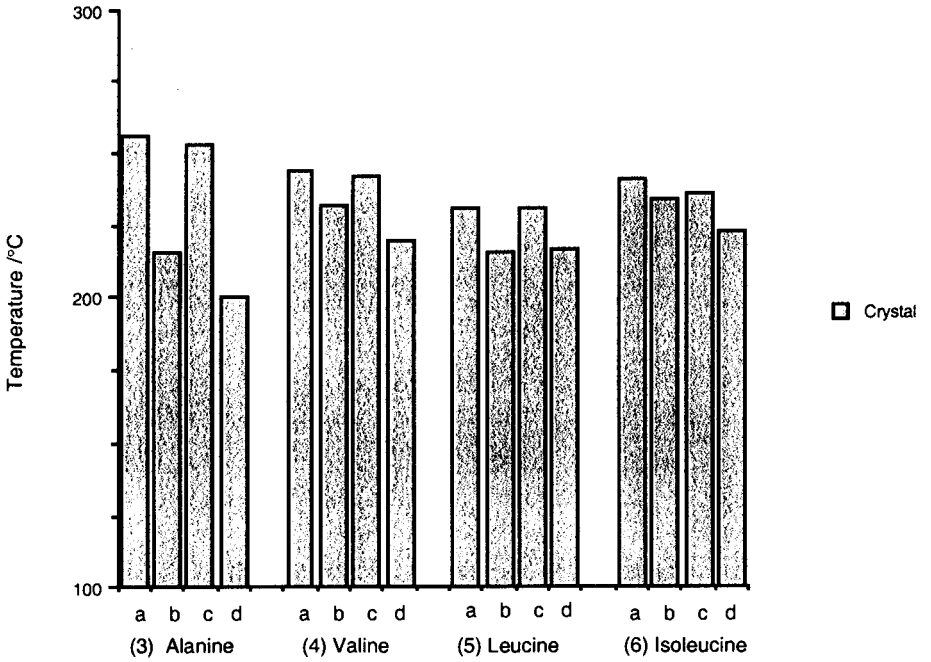


Fig. 2. Phase behaviour, compounds **3**, **4**, **5** and **6**, grouped by amino acid.

seen that the latter complexes exhibit smectic A phases and nematic mesophases at lower temperatures. This is illustrated by the smectic A phase seen for the **c** ($n = 7$, $m = 7$) compound at 140°C [32], while for the alanine complex with the same size Schiff base the phase is seen at 231°C. The effect is even greater for the ^{n}Bu(acac) derivative, where a smectic A phase is seen at 78°C [33], or for the analogous cyclopentadiene complex, where the smectic phase was seen at 92°C [32]. We tentatively ascribe the higher transition temperatures observed in the amino acid complexes to intermolecular hydrogen bonding interactions, which cause greater attractions between the individual molecules in the crystal phase and hence lead to an increase in the melting point.

One previous report deals with the mesogenic behaviour of amino acid complexes of palladium [39]. Here, very long chains on azo benzene and Schiff base units (14 carbons on each end) resulted in relatively low-melting mesogens (90–100°C) exhibiting smectic C and A phases. Given the more compact nature of our central core, our higher transition temperatures are unsurprising.

Thus it can be seen that our results are consistent with established precedent: compared with the acac group, amino acids increase the melting points of the complexes. While the natural amino acids might appear to be an attractive way to introduce chirality into metallomesogens, given the problems associated with the higher transition temperatures that they induce, they will probably not become popular motifs in metallomesogen chemistry.

4. Experimental

4.1. General

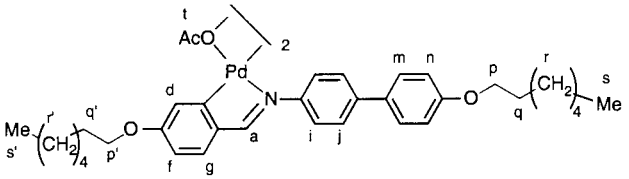
All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on either a Bruker Avance 300 or on an Avance 400 in $CDCl_3$ and are referenced to external TMS, assignments being made with the use of decoupling, nOe and the DEPT and COSY pulse sequences. Thermal analyses were performed on 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. The 4-alkyloxy-*N*-(4′-alkyloxybiphenyl)benzylidenes were prepared as previously described [32].

4.2. Preparation of ortho-metallated palladium acetate complexes (2a–d)

Compound **2c** is described in detail; all other homologues were prepared similarly.

Benzylidene **1c** (0.41 g, 8.5×10^{-4} mol) and palladium acetate (0.191 g, 8.5×10^{-4} mol) were dissolved in acetic acid (250 ml) at 60°C, and stirred (20 h). The solvent was removed, the crude product was dissolved in chloroform, filtered to remove traces of palladium black and the yellow solution was evaporated to dryness.

Yield 0.55 g (98%, 4.2×10^{-4} mol). NMR data:



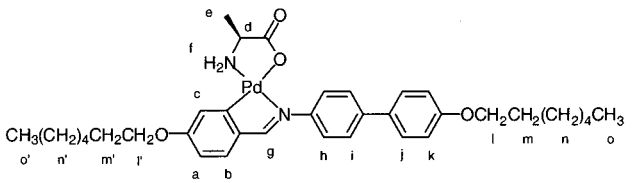
δ_H: 7.59 (1H, s, H_a), 7.51 (2H, AA′XX′, $J = 8$ Hz, H_m), 7.35 (2H, AA′XX′, $J = 8$ Hz, H_j), 7.18 (1H, d, ^3J(HH) 8.4 Hz, H_g), 6.95 (2H, AA′XX′, $J = 8$ Hz, H_n), 6.78 (2H, AA′XX′, $J = 8$ Hz, H_i), 6.59 (1H, dd, ^3J(HH) 8.4 Hz, ^4J(HH) 2.3 Hz, H_f), 6.03 (1H, d, ^4J(HH) 2.3 Hz, H_d), 4.05 (2H, t, ^3J(HH) 6.4 Hz, $H_{p'}$), 4.00 (2H, t, ^3J(HH) 6.7 Hz, H_p), 1.90 (3H, s, H_t), 1.81 (4H, m, $H_{q,q'}$), 1.40 (16H, m, $H_{r,r'}$), 0.88 (6H, t, ^3J(HH) 7.1 Hz, $H_{s,s'}$).

4.3. Preparation of palladium(alanine) [4-heptyloxy-N-(4′-heptyloxybiphenyl) benzylidene] (3c)

Compound **3c** is described in detail; all other homologues were prepared similarly.

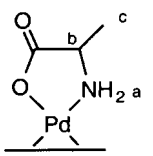
Alanine (0.051 g, 5.69×10^{-4} mol) was added to a solution of the acetate bridged **2c** complex (0.370 g, 2.84×10^{-4} mol) in methanol (150 ml). This solution was stirred at 70°C for 4 h. A colour change, from an opaque orange to translucent yellow, signalled completion of the reaction. The solvent was removed and the crude product was redissolved in chloroform and filtered through Celite. Purification was achieved using column chromatography on silica eluting with a 9:1 mixture of chloroform and methanol.

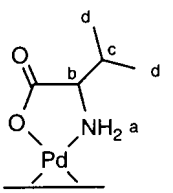
Yield 0.312 g (82%, 4.67×10^{-4} mol). NMR data:



δ_H: 7.95 (1H, s, H_g), 7.39 (2H, AA′XX′, $J = 8$ Hz, H_i), 7.36 (2H, AA′XX′, $J = 8$ Hz, H_j), 7.30 (1H, AA′XX′, $J = 8$ Hz, H_h), 7.29 (1H, d, H_b), 6.91 (2H, AA′XX′, $J = 8$ Hz, H_k), 6.58 (1H, dd, H_a), 6.25 (1H, d, H_c), 4.47 (1H, br, H_f), 3.97 (2H, t, $H_{l'}$), 3.86 (2H, t, H_l), 3.77 (1H, m, H_d), 2.87 (1H, br, H_f), 1.8 (4H, m, $H_{m,m'}$), 1.64 (3H, m, H_e), 1.32 (16H, m, $H_{n,n}$), 0.88 (6H, m, $H_{o,o'}$).

NMR signals specific to the different amino acids:

Alanine  4.44 (1H, br, H_a), 3.77 (1H, m, H_b), 2.86 (1H, br, H_a), 1.19 (3H, m, H_c)

Valine  4.59 (1H, br, H_a), 3.51 (1H, m, H_b), 2.55 (1H, br, H_a), 0.99 (1H, m, H_c), 0.95 (6H, m, H_d)

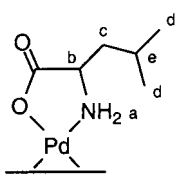
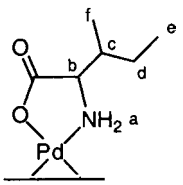
Leucine  4.70 (1H, br, H_a), 3.70 (1H, m, H_b), 2.53 (1H, br, H_a), 1.54 (2H, m, H_c), 1.05 (1H, m, H_d), 0.98 (6H, m, H_e)

Table 2
Elemental analysis data for compounds **3**, **4**, **5** and **6**

Compound	C (%)		H (%)		N (%)	
	Found	Expected	Found	Expected	Found	Expected
3a	60.3	60.1	6.1	6.1	4.5	4.7
3b	63.1	63.2	7.1	7.0	4.3	4.2
3c	63.1	63.7	7.1	7.1	3.8	4.1
3d	64.2	64.9	7.6	7.6	3.6	3.9
4a	61.3	61.7	6.4	6.5	4.3	4.5
4b	63.1	63.2	7.1	7.0	4.3	4.2
4c	64.2	64.5	7.1	7.1	3.8	4.1
4d	65.5	65.7	7.9	7.8	3.2	3.7
5a	61.9	62.2	6.6	6.6	4.4	4.4
5b	62.7	63.7	7.4	7.1	3.9	4.1
5c	64.5	64.9	7.4	7.6	3.6	3.9
5d	65.7	66.1	7.8	7.9	3.4	3.7
6a	62.0	62.2	6.6	6.6	4.2	4.4
6b	63.0	63.7	7.1	7.1	3.9	4.1
6c	64.8	64.9	7.5	7.6	3.7	3.9
6d	65.7	66.1	7.8	7.9	3.6	3.7

Isoleucine 

(4.54 (1H, br, H_a), 3.60 (1H, m, H_b), 2.54 (1H, br, H_a), 1.53 (1H, m, H_c), 1.3 (2H, m, H_d), 1.15 (3H, m, H_f), 0.96 (3H, m, H_e)

The mesogenic behaviour of all homologues is summarised in Fig. 2 and detailed in Table 1. Elemental analyses are detailed in Table 2.

Acknowledgements

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