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Cyclopalladated Schiff's base liquid crystals: the effect of the acac group on the thermal behaviour

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Abstract

The cyclopalladation of mesogenic Schiff's bases and subsequent reaction with a β-diketone yields novel metallomesogens. In particular, use of simple alkyl substituted diketones can have a very dramatic effect on both the melting and clearing point.

Keywords: Cyclopalladation; Liquid crystals; Mesogenic

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], and cyclopalladated compounds have proved to be a particularly fertile area of research, with many different examples from many different groups [7–19].

In previous papers [20,21] we have described the effect of a cyclopentadienyl group upon the mesogenic behaviour of a series of mono-cyclopalladated complexes, and the effect of two cyclometallated units on mesogenic behaviour. Here we present the results of using a variety of different β-diketonate ligands on a series of mono-cyclopalladated complexes.

1. Synthesis

The synthesis of the new compounds described here, (**3**) and (**4**), 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 [20], the β-diketones were synthesised in high yield via a literature route. [22] The cyclopalladation step to give the intermediate (**2**) was essentially quantitative, and (**2**) was used without further purification. The synthesis of the symmetrical diketonate derivatives (**3**) ($R = R' = $ Me, ^{t}Bu, ^{n}Bu, ^{n}hexyl and ^{n}octyl) and the unsymmetric derivatives (**4**) ($R = $ Me, $R' = {}^{t}$Bu, ^{n}Bu, ^{n}hexyl and ^{n}octyl) proceeded in good yield, and these complexes were purified by column chromatography. All homologues of compounds (**3**) and (**4**) were analysed by ^{1}H and ^{13}C NMR and gave good elemental analyses (Table 2). In all, four different Schiff's bases and eight different β-diketones were used, giving rise to 32 new compounds. It should be noted that reaction of the intermediates (**2**) with the unsymmetrical β-diketones to give complexes (**4**) gives rise to two isomeric products, Scheme 2. The relative quantities of the two isomers was determined by proton NMR. The signals for the immine protons (7.46 and 7.45 ppm) and the signals for the methyl groups of the diketone (2.06 and 1.90 ppm) in the two isomers are clearly distinguishable. To the accuracy of the NMR machine, integration shows both isomers to be present in equal quantities.

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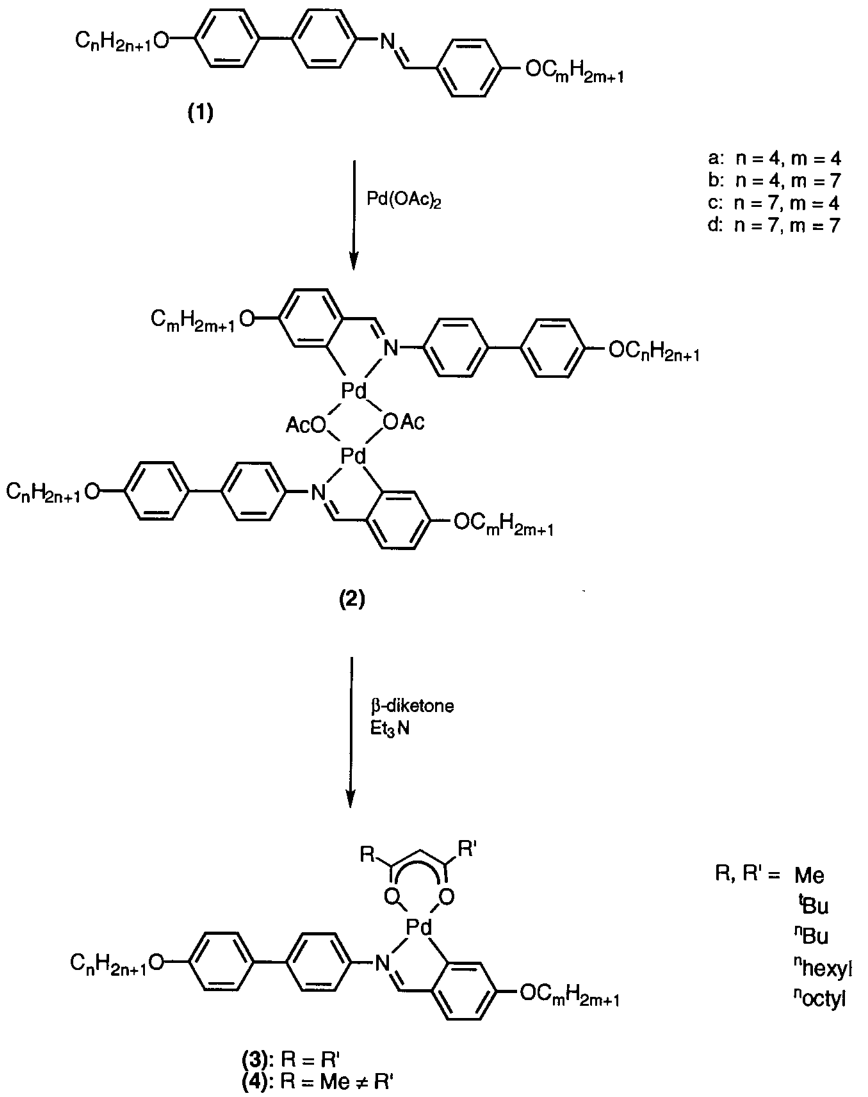


Scheme 1.

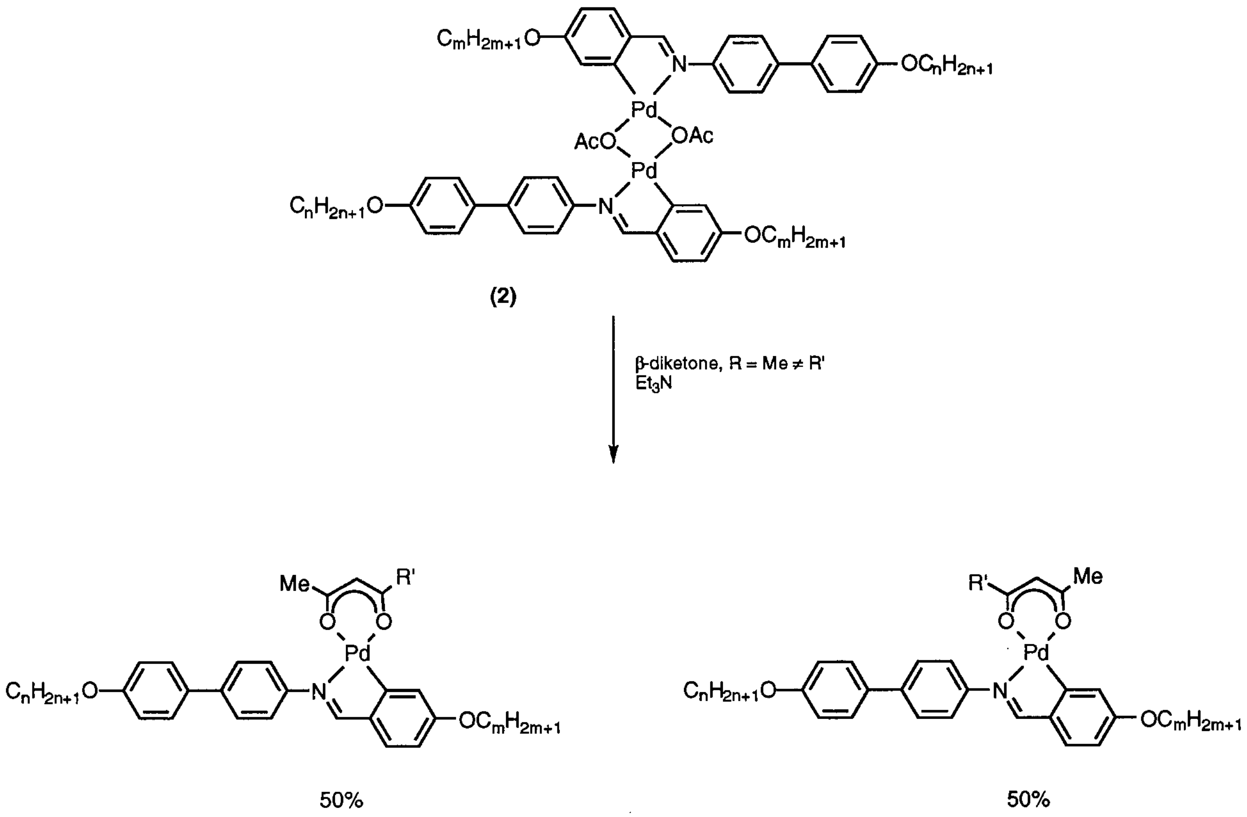
2. Thermal properties

The thermal behaviour of the diketonate complexes (**3**) and (**4**) is comprehensively detailed in Table 1 and summarised in Figs. 1 and 2. Thus, with one exception, all the complexes with ^{n}alkyl chains showed a smectic A phase and many also exhibited a nematic phase before clearing. The exception showed only a nematic phase. The phases were identified on the basis of their optical texture. The nematic phase exhibited schlieren textures, showing both 4 and 2 point brushes. The smectic A phase appeared as a focal-conic fan texture which separated on cooling as battonets which consisted of growing focal-conic domains. Though exhaustive differential scanning calorimetry (DSC) measurements were not undertaken, DSC data for representative examples were recorded: this data is incorporated into Table 1.

Figs. 1 and 2 summarise the thermal behaviour in two different ways. Fig. 1 shows the thermal behaviour of the compounds grouped according to the Schiff's base unit present, and only includes the data for the straight chain diketonates (i.e. the not the data for the ^{t}Bu complexes). In contrast, Fig. 2 shows the thermal behaviour of the compounds grouped according to the diketone used. Fig. 2 includes all the data present in Table 1.

If we ignore the ^{t}Bu complexes for the moment, it is immediately apparent from Fig. 1 that any diketone brings the both the melting and clearing points down substantially (around 50 K on average, and 100 K in some cases) compared with the simple acac.

Fig. 1 clearly shows that compounds (**4**) with unsymmetrical diketones have melting points substantially lower (some 50 K) than their symmetrical homologues (**3**). Whilst this could be accounted for by the fact that compounds (**4**) are in fact mixtures of two isomers



Scheme 2.

(Scheme 2) and thus what we are seeing here is a manifestation of the eutectic effect, it is likely that the inherent asymmetry of compounds (**4**) is in fact responsible for their reduced melting points. Compounds (**4**) always have a higher clearing point their analogous compound (**3**) with the same R′ group.

As we move to compounds with longer chains, we see a stabilisation of the smectic A phase at the expense of the nematic. This well known effect [23] is shown with increasing chain length on both the diketone and the Schiff's base unit. Thus, both Figs. 1 and 2 show the dominance of the smectic phase towards the right hand side of the graphs.

Fig. 2 indicates that the greatest nematic stability is shown by the compounds with ^{n}butyl chains attached to the diketone. Thus both compounds (**3**) (R = R′ = ^{n}Bu) and compounds (**4**) (R = Me, R′ = ^{n}Bu) have greater nematic ranges than the parent simple acac compounds (**3**) (R = R′ = Me). In particular, these compounds (**4**) (R = Me, R′ = ^{n}Bu) all show nematic phases, with the Schiff's base derivative with the shortest chains showing only a nematic phase.

It is interesting to note from Fig. 1 that compounds (**b**) (**3** and **4**) ($n = 4$, $m = 7$) and compounds (**c**) (**3** and **4**) ($n = 7$, $m = 4$) show very similar phase behaviour. Another interesting feature apparent from Fig. 2 is that for compounds (**4**), the (**b**) and (**c**) derivatives have much reduced melting points compared with the (**a**) and (**d**) derivatives. The first observation seems to imply that within any one compound the combined length of the alkyloxy chains on the Schiff's base is more important than the distribution. The second observation is perhaps best accounted for by the fact that compounds (**a**) and (**d**) have their rigid aromatic cores symmetrically substituted by their alkyloxy chains and thus any asymmetry that arises from head to tail or head to head packing has minimal effect on the melting point.

The effect of using the ^{t}Bu diketone is very marked. The sterically demanding group destabilises any mesogenic behaviour to such an extent that only monotropic behaviour is seen. Monotropic nematic phases are seen for all four compounds studied, with the clearing points around 130°C, some 50–120° lower than the other compounds. The melting point of these compounds is substantially higher than their normal chain analogues, indicating that the less conformationally disordered ^{t}Bu groups result in a better crystal packing. For two of these compounds a monotropic smectic C phase was observed below the nematic, the transition occurring some 30° below the clearing point. It is interesting to note that this was a tilted C phase, rather than the smectic A phase shown by the normal chain analogues.

Table 1
Mesogenic Behaviour of Compounds (**3**) and (**4**)

n	*m*	R	R′	*trans*	*T* (°C)	Δ*H* (J g^{-1})	*trans*	*T* (°C)	Δ*H* (J g^{-1})	*trans*	*T* (°C)	Δ*H* (J g^{-1})
4	4	Me	Me	K–S_A	184		S_A–N	209		N–I	260	
4	4	Me	^{n}Bu	K–S_A	130		S_A–N	147		N–I	225	
4	4	^{n}Bu	^{n}Bu	K–N	131	31.9	N–I	195	2.6			
4	4	Me	^{n}hex	K–S_A	130	34.4	S_A–N	182	1.3	N–I	210	1.6
4	4	^{n}hex	^{n}hex	K–S_A	139		S_A–N	158		N–I	188	
4	4	Me	^{n}oct	K–S_A	139	28.5	SA–N	198	1.6	N–I	210	1.2
4	4	^{n}oct	^{n}oct	K–S_A	137		S_A–I	176				
4	4	^{t}Bu	^{t}Bu	K–I	205		N–I	127[a]				
4	7	Me	Me	K–S_A	162		S_A–N	241		N–I	261	
4	7	Me	^{n}Bu	K–S_A	101	34.3	S_A–N	164	1.2	N–I	206	1.1
4	7	^{n}Bu	^{n}Bu	K–S_A	129	(33.2	S_A–N	134	—[b])	N–I	198	1.8
4	7	Me	^{n}hex	K–S_A	71	38.0	S_A–N	201	1.9	N–I	220	1.4
4	7	^{n}hex	^{n}hex	K–S_A	121		S_A–N	178		N–I	182	
4	7	Me	^{n}oct	K–S_A	88		S_A–N	198		N–I	208	
4	7	^{n}oct	^{n}oct	K–S_A	134	27.4	S_A–I	199	3.4			
4	7	^{t}Bu	^{t}Bu	K–I	199		N–I	124[a]				
7	4	Me	Me	K–S_A	155		S_A–N	225		N–I	249	
7	4	Me	^{n}Bu	K–S_A	76		S_A–N	184		N–I	211	
7	4	^{n}Bu	^{n}Bu	K–S_A	117	30.0	S_A–N	138	1.4	N–I	181	1.4
7	4	Me	^{n}hex	K–S_A	76	30.2	S_A–N	201	1.3	N–I	205	1.3
7	4	^{n}hex	^{n}hex	K–S_A	116		S_A–N	176		N–I	183	
7	4	Me	^{n}oct	K–S_A	85	32.6	S_A–N	210	(3.0	N–I	212	—[b])
7	4	^{n}oct	^{n}oct	K–S_A	135		S_A–I	198				
7	4	^{t}Bu	^{t}Bu	K–I	224		S_C–N	101[a]		N–I	131[a]	
7	7	Me	Me	K–S_A	141		S_A–I	245				
7	7	Me	^{n}Bu	K–S_A	78		S_A–N	199		N–I	212	
7	7	^{n}Bu	^{n}Bu	K–S_A	109	28.9	S_A–N	161	(2.7	N–I	187	—[b])
7	7	Me	^{n}hex	K–S_A	130	35.7	S_A–I	208	2.9			
7	7	^{n}hex	^{n}hex	K–S_A	115	36.5	S_A–N	179	1.6	N–I	182	2.4
7	7	Me	^{n}oct	K–S_A	118		S_A–I	206				
7	7	^{n}oct	^{n}oct	K–S_A	128	34.7	S_A–I	190	3.8			
7	7	^{t}Bu	^{t}Bu	K–I	205		S_C–N	107[a]		N–I	134[a]	

[a] Monotropic tranisition.

[b] Combined enthalpies.

3. Conclusions

These results clearly show the advantages of using short chain length ^{n}alkyl diketones: both melting and clearing points can be brought down substantially. In addition, it appears that the effect of a short (four carbon, ^{n}Bu) alkyl chain substantially stabilises the nematic phase at the expense of the smectic A phase. This can be understood in terms of the short chain freely moving at the side of the rigid core disrupting both the crystal packing and the lateral interactions that are necessary for the formation of a smectic phase. These short chained alkyl diketones bring the melting and clearing points down to a similar extent to that observed with the cyclopentadienyl group, which we used in analogous compounds [20] (the effect is to make the molecule non-planar, disrupting the packing and thus bringing down the melting and clearing points). The short chain diketones are to be preferred, however, as the thermal stability of their palladium complexes is much greater than that of the cyclopentadienyl compounds (where decomposition can set in at 200°C). In contrast, when a ^{t}Bu group is attached to the acac core, the mesophases are destabilised very substantially, to the extent that all mesophases exhibited are monotropic. The ^{t}Bu group is a compact group that cannot move freely, and will not disrupt the packing forces.

Other analogous work has used both simple acac and phenyl substituted [24] β-diketonate complexes of palladium Schiff's base derivatives. At the time, these simple acac compounds were unusual in that they showed nematic phases [9]. Our new results complement these older results, with our short chain diketones showing a greatly stabilised nematic phase. Indeed, we have also shown this effect with some of our di-metallated complexes [21].

Though, one report [25] is solely concerned with the synthesis of 3-substituted pentane-2,4-diones for the purposes of liquid crystal research, apart from two recent papers [19,21] there have been no other reports of the use of the simple alkyl diketones that we have employed to our very great advantage.

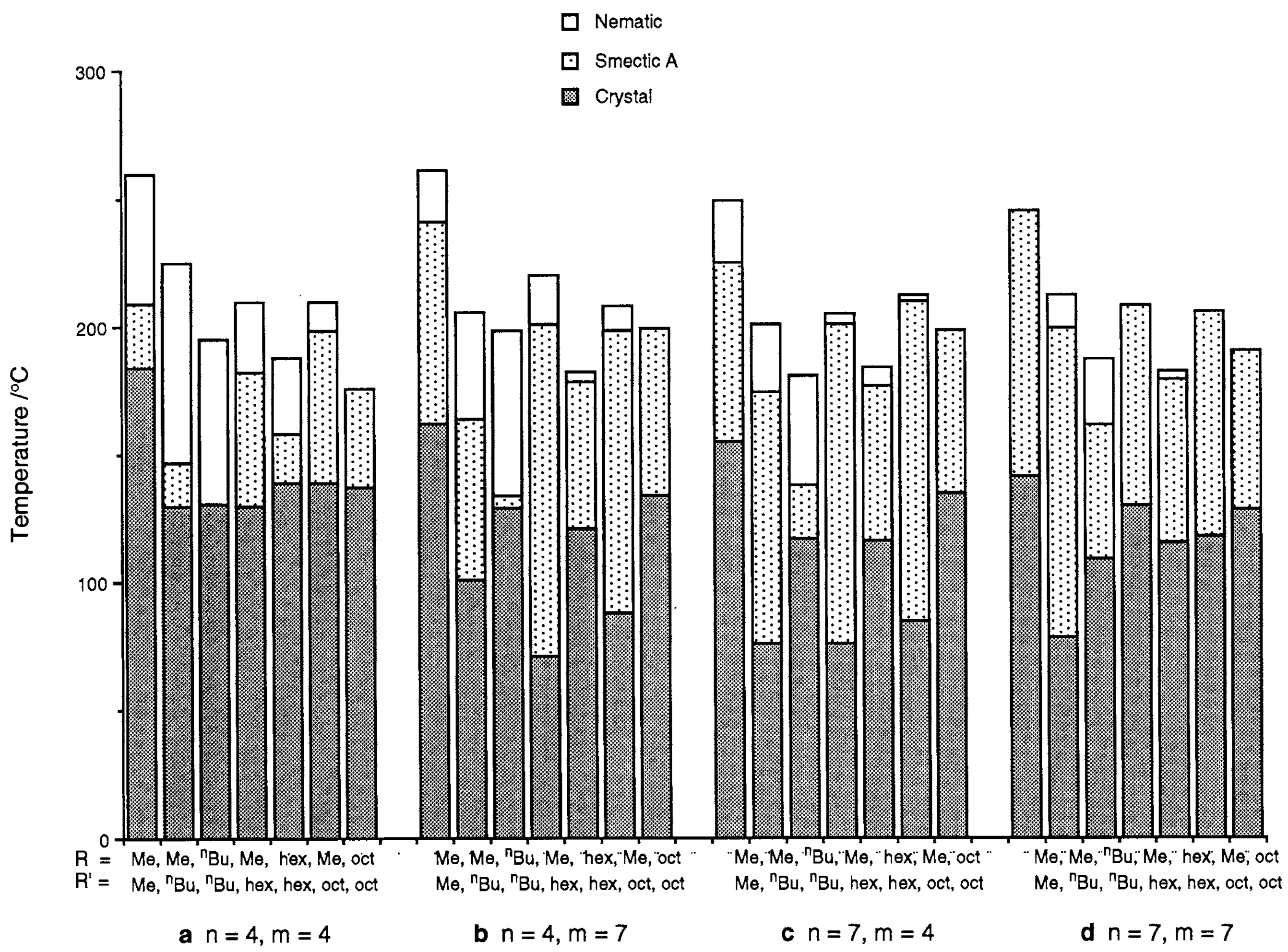


Fig. 1. Phase behaviour of compounds (3) and (4) grouped by Schiff's base.

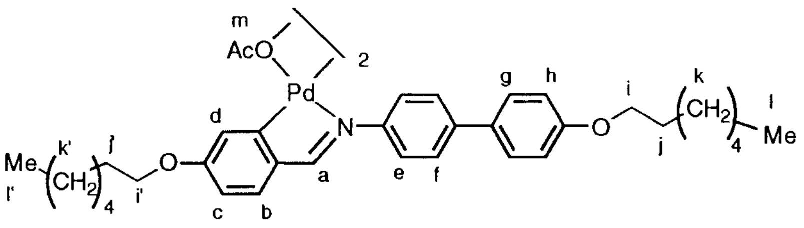
4. Experimental

4.1. General

All chemicals were used as supplied, unless noted otherwise. All NMR spectra were obtained on either a Bruker AC250 or on an AC400 in $CDCl_3$ and are referenced to external TMS, assignments being made with the use of decoupling, nOe and the COSY pulse sequence. 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. 4-Alkyloxy-*N*-(4′-alkyloxybiphenyl)benzylidenes were synthesised via literature routes [20]. All β-diketones with the exception of 2,2,6,6-tetramethyl-3,5-heptanedione (which is commercially available) were synthesised via literature routes [22].

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

(**2d**) is described in detail, all other homologues were prepared similarly. 4-Heptyloxy-*N*-(4′-heptyloxybiphenyl)benzylidene (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 dissolved in chloroform, filtered to remove traces of palladium black and the yellow solution evaporated to dryness.



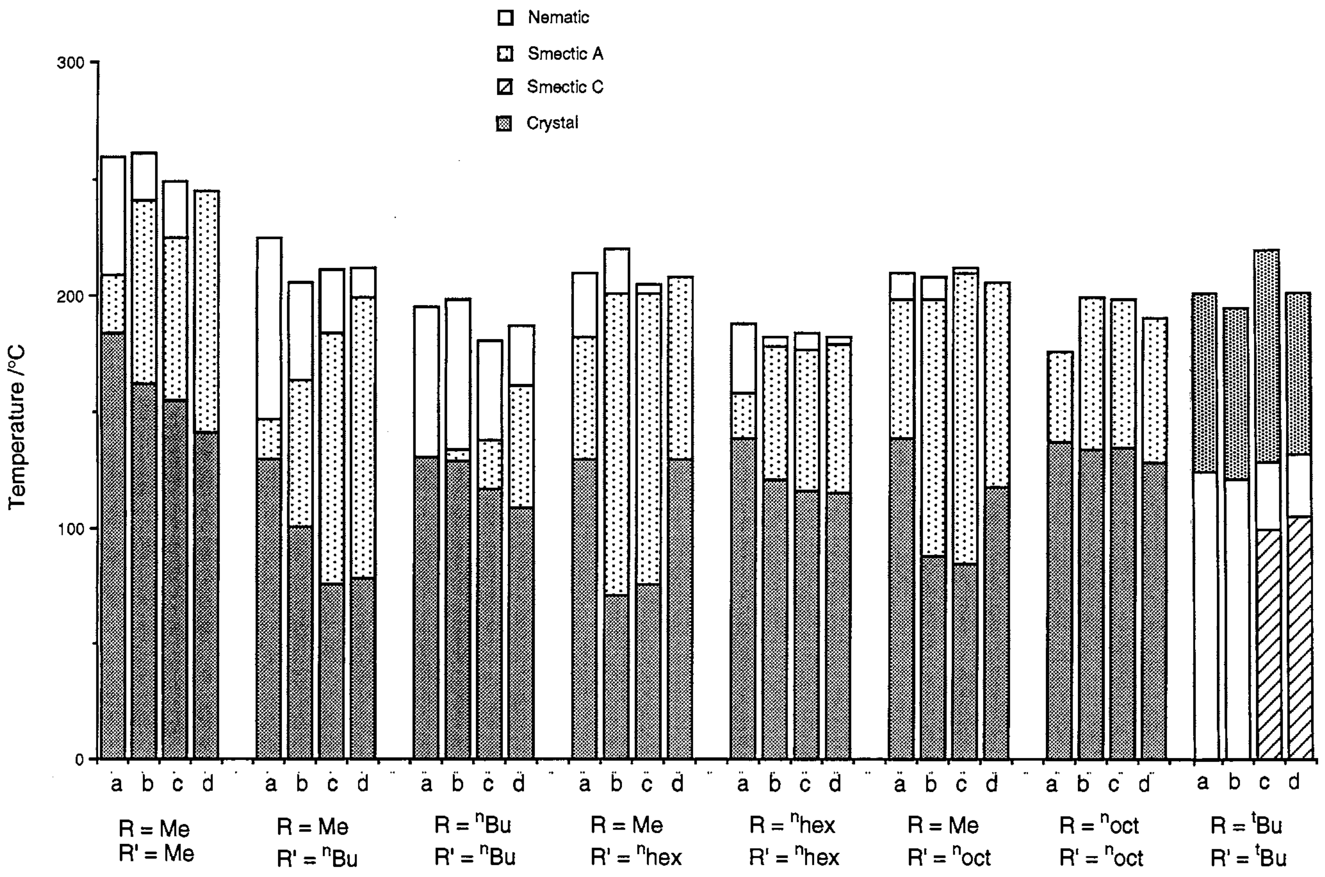


Fig. 2. Phase behaviour of compounds (**3**) and (**4**) grouped by diketone.

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′, H_g), 7.35 (2H, AA′XX′, H_f), 7.18 (1H, d, ^3J(HH) 8.4 Hz, H_b), 6.95 (2H, AA′XX′, H_h), 6.78 (2H, AA′XX′, H_e), 6.59 (1H, dd, ^3J(HH) 8.4 Hz, ^4J(HH) 2.3 Hz, H_c), 6.03 (1H, d, ^4J(HH) 2.3 Hz, H_d), 4.05 (2H, t, ^3J(HH) 6.4 Hz, $H_{i'}$), 4.00 (2H, t, ^3J(HH) 6.7 Hz, H_i), 1.90 (3H, s, H_m), 1.81 (4H, m, $H_{j,j'}$), 1.40 (16H, m, $H_{k,k'}$), 0.88 (6H, t, ^3J(HH) 7.1 Hz, $H_{l,l'}$)

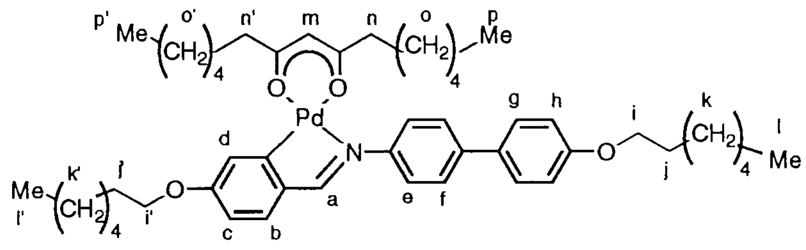
4.3. Preparation of β-diketonate palladium complexes (3) and (4)

(**3d**) with R = R′ = ⁿhex is described in detail, all other homologues were prepared similarly.

7,9-Pentadecanedione (0.081 g, 3.39×10^{-4} mol) and triethylamine (0.034 g, 3.39×10^{-4} mol) were added to a solution of the acetate bridged palladium complex (**2d**), (0.200 g, 1.54×10^{-4} mol) in acetone (150 ml) at room temperature and stirred (2 h). The solvent was removed and the product was purified by column chromatography on silica, eluting with a 50/50 mixture of dichloromethane and hexane.

Yield 0.208g (76%, 2.34×10^{-4} mol)

NMR data (**3**):



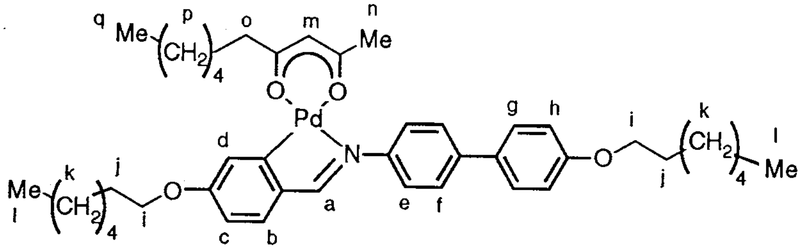
δ_H: 8.06 (1H, s, H_a), 7.55 (2H, AA′XX′, H_f), 7.52 (2H, AA′XX′, H_g), 7.45 (2H, AA′XX′, H_e), 7.32 (1H, d, ^3J(HH) 8.5 Hz, H_b), 7.19 (1H, d, ^4J(HH) 2.3 Hz, H_d), 6.97 (2H, AA′XX′, H_h), 6.63 (1H, dd, ^3J(HH) 8.5, ^4J(HH) 2.3 Hz, H_c), 5.33 (1H, s, H_m), 4.09 (2H, t, ^3J(HH) 6.0 Hz, $H_{i'}$), 4.00 (2H, t, ^3J(HH) 6.0 Hz, H_i), 2.32 (2H, t, ^3J(HH) 7.5 Hz, $H_{n'}$), 2.14 (2H, t, ^3J(HH) 7.5 Hz, H_n),

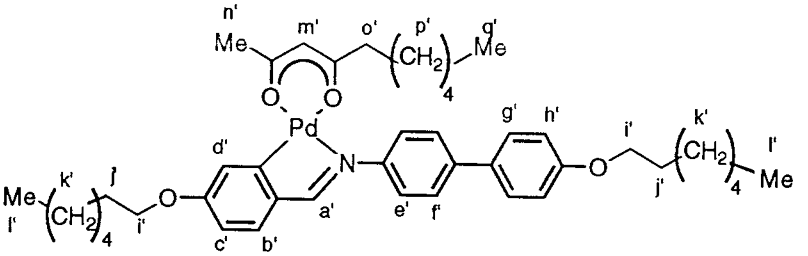
Table 2
Elemental Analysis data for Compounds (**3**) and (**4**)

n	*m*	R	R′	C %		H %		N %	
				Found	(Expected)	Found	(Expected)	Found	(Expected)
4	4	Me	^{n}Bu	64.4	(64.9)	6.8	(6.7)	2.2	(2.2)
4	4	^{n}Bu	^{n}Bu	65.8	(66.1)	7.1	(7.2)	2.2	(2.0)
4	4	Me	^{n}hex	65.4	(65.7)	7.1	(7.0)	2.1	(2.1)
4	4	^{n}hex	^{n}hex	67.5	(67.6)	7.7	(7.7)	1.9	(1.9)
4	4	Me	^{n}oct	66.5	(66.5)	7.5	(7.3)	2.0	(2.0)
4	4	^{n}oct	^{n}oct	67.0	(67.5)	7.6	(7.7)	2.0	(1.9)
4	4	^{t}Bu	^{t}Bu	65.7	(66.1)	7.1	(7.2)	2.0	(2.0)
4	7	Me	^{n}Bu	65.9	(66.1)	7.3	(7.2)	2.1	(2.0)
4	7	^{n}Bu	^{n}Bu	67.2	(67.2)	7.5	(7.6)	1.7	(1.9)
4	7	Me	^{n}hex	66.8	(66.9)	7.5	(7.4)	2.0	(2.0)
4	7	^{n}hex	^{n}hex	69.1	(68.6)	8.3	(8.1)	1.5	(1.8)
4	7	Me	^{n}oct	67.6	(67.6)	7.5	(7.7)	1.7	(1.9)
4	7	^{n}oct	^{n}oct	69.5	(69.7)	8.5	(8.5)	1.5	(1.7)
4	7	^{t}Bu	^{t}Bu	67.4	(67.2)	7.6	(7.6)	2.0	(1.9)
7	4	Me	^{n}Bu	66.0	(66.1)	7.2	(7.2)	2.2	(2.0)
7	4	^{n}Bu	^{n}Bu	67.3	(67.3)	7.5	(7.6)	2.1	(1.9)
7	4	Me	^{n}hex	66.7	(66.9)	7.5	(7.4)	1.8	(2.0)
7	4	^{n}hex	^{n}hex	68.4	(68.6)	8.0	(8.1)	1.8	(1.8)
7	4	Me	^{n}oct	67.3	(67.6)	7.6	(7.7)	2.1	(1.9)
7	4	^{n}oct	^{n}oct	69.2	(69.7)	8.2	(8.5)	1.5	(1.7)
7	4	^{t}Bu	^{t}Bu	67.3	(67.3)	7.8	(7.6)	1.7	(1.9)
7	7	Me	^{n}Bu	67.0	(67.3)	7.7	(7.6)	2.0	(1.9)
7	7	^{n}Bu	^{n}Bu	68.7	(68.3)	7.8	(7.9)	1.7	(1.8)
7	7	Me	^{n}hex	67.9	(67.9)	7.7	(7.8)	1.7	(1.8)
7	7	^{n}hex	^{n}hex	69.4	(69.4)	8.3	(8.4)	1.7	(1.7)
7	7	Me	^{n}oct	68.3	(68.6)	8.0	(8.1)	1.7	(1.8)
7	7	^{n}oct	^{n}oct	67.0	(70.5)	8.6	(8.8)	1.5	(1.6)
7	7	^{t}Bu	^{t}Bu	68.5	(68.3)	7.7	(7.9)	1.9	(1.8)

1.77 (4H, m, $H_{j,j'}$), 1.5–1.2 (32H, m, $H_{k,k',o,o'}$), 0.90 (6H, $H_{l,l'}$), 0.80 (6H, $H_{p,p'}$)

NMR data (**4**):





δ_H: 8.05 (1H, s, $H_{a/a'}$), 8.04 (1H, s, $H_{a/a'}$), 7.56 (2H, AA′XX′, $H_{f/f'}$), 7.55 (2H, AA′XX′, $H_{f/f'}$), 7.53 (2H, AA′XX′, $H_{g/g'}$), 7.52 (2H, AA′XX′, $H_{g/g'}$), 7.46 (2H, AA′XX′, $H_{e/e'}$), 7.45 (2H, AA′XX′, $H_{e/e'}$), 7.32 (1H, d, ^{3}J(HH) 8.0 Hz, $H_{b/b'}$), 7.28 (1H, d, ^{3}J(HH) 8.0 Hz, $H_{b/b'}$), 7.17 (1H, d, ^{4}J(HH) 2.3 Hz, $H_{d/d'}$), 7.16 (1H, d, ^{4}J(HH) 2.3 Hz, $H_{d/d'}$), 6.98 (4H, AA′XX′, $H_{h,h'}$), 6.63

(1H, dd, ${}^{3}J$(HH) 8.0, ${}^{4}J$(HH) 2.3 Hz, $H_{c/c'}$), 6.62 (1H, dd, ${}^{3}J$(HH) 8.0, ${}^{4}J$(HH) 2.3 Hz, $H_{c/c'}$), 5.35 (2H, s, $H_{m,m'}$), 4.10 (4H, t, ${}^{3}J$(HH) 6.0 Hz, $H_{i/i'}$), 4.01 (4H, t, ${}^{3}J$(HH) 6.0 Hz, $H_{i,i'}$), 2.32 (2H, t, ${}^{3}J$(HH) 7.5 Hz, $H_{o/o'}$), 2.14 (2H, t, ${}^{3}J$(HH) 7.5 Hz, $H_{o/o'}$), 2.06 (3H, s, $H_{n/n'}$), 1.90 (3H, s, $H_{n/n'}$), 1.77 (8H, m, $H_{j,j'}$), 1.5–1.2 (48H, m, $H_{k,k',p,p'}$), 0.85 (18H, m, $H_{l,l',q,q'}$)

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

Acknowledgements

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