Effect of the Position and Number of Chiral Carbons on Ferroelectric Liquid Crystals from Multichain Mononuclear *ortho*-Palladated Complexes

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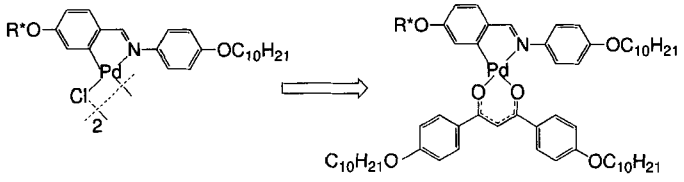
Abstract: A series of twelve mononuclear *ortho*-palladated complexes incorporating a Schiff base and a β-diketone ligand have been synthesised. These compounds have four nonequivalent terminal chain positions and differ in the number and position(s) of chiral chains [(*R*)-2-methylheptyl] in the structure. A study of the ferroelectric properties of the compounds has been performed. It is found that the spontaneous polarisation is highly dependent not only on the number of chiral carbons present, but also on the

Keywords
ferroelectrics · liquid crystals · metallomesogens · palladium complexes



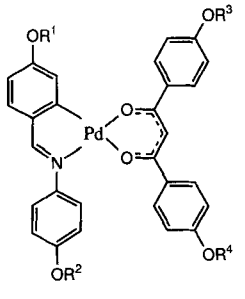
K 114 (S_C 111) S_A 118 I

In recent years interest in metal-containing liquid crystals has been increasing, and several review articles have appeared describing this field.[1] Investigation into ferroelectricity in metallomesogens (metal-containing liquid crystals) is a relatively recent development, and the first transition-metal compound to exhibit ferroelectric behaviour was reported in 1989.[2] Since this first example, a number of other compounds have been reported, including paramagnetic ferroelectric copper(II), vanadium(IV) and palladium salicylaldiminates,[3] mononuclear β-diketonate *ortho*-palladated imines,[4] and dimeric chloro-bridged *ortho*-palladated imine complexes containing either two or four chiral chains.[5]

The most common problem associated with metal-containing mesogens is the high transition temperatures often encountered. At these elevated temperatures thermal decomposition often occurs, which hinders the study of the physical properties of the mesophases. An approach that has been successfully applied to obtain systems with lower transition temperatures is the synthesis of molecules with less symmetrical shapes.[6] On changing from a dinuclear to a mononuclear complex, reductions of around 100 °C in the clearing points are obtained (Fig. 1).

The mononuclear complex shown in Figure 1 is of particular interest because it combines relatively low transition temperatures with the possibility of incorporating chiral carbons in different positions. The aim of the work described here was to synthesise a series of twelve mononuclear mixed-ligand palladium complexes covering all possible permutations for the incorporation of one, two, three or four chiral chains (see Fig. 2), in order to study the effect of the position and number of chiral carbons on the liquid crystalline and ferroelectric properties of the compounds.

This is the first time, in metallomesogens or in purely organic liquid crystalline systems, that the influence of chiral substituents in four nonequivalent positions has been studied systematically.



3	C_{10} C_8* C_{10} C_{10}
4[a]	C_{10} C_{10} C_8* C_{10}
5	C_8* C_8* C_{10} C_{10}
6[a]	C_8* C_{10} C_8* C_{10}
8	C_{10} C_{10} C_8* C_8*
9[a]	C_8* C_8* C_8* C_{10}
10	C_{10}* C_8 C_8* C_8*
11	C_{10} C_8* C_8* C_8*
12	C_8* C_8* C_8* C_8*

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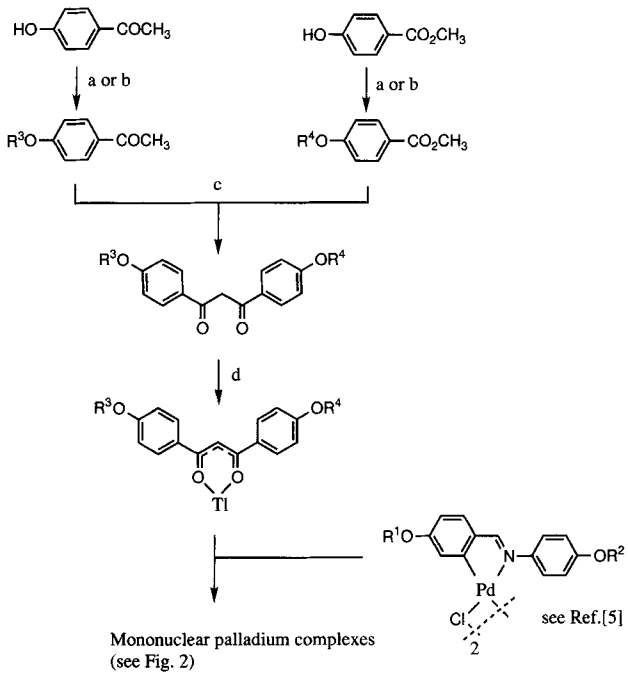
Results and Discussion

Synthesis: The chloro-bridged dimeric palladium precursors were prepared and characterised according to the literature procedure.[5] The synthesis of the thallium β-diketonates and the subsequent synthesis of the mononuclear complexes is outlined in Scheme 1.



Scheme 1. Synthesis of mononuclear palladium complexes in Figure 2. a) Williamson etherification with $CH_3(CH_2)_9Br$ or b) Mitsunobu reaction with $CH_3(CH_2)_5$*$CH(OH)CH_3$, TPP and DEAD; c) NaH [8]; d) TlOEt [9]. For final coupling step, see Experimental Procedure.

4-Decyloxyacetophenone and methyl 4-decyloxybenzoate were obtained by Williamson etherification of 4-hydroxyacetophenone and methyl 4-hydroxybenzoate, respectively (Scheme 1a). The chiral chains were introduced by means of the Mitsunobu reaction[7] between the appropriate phenol derivative and (*S*)-2-octanol (Aldrich), triphenylphosphine and diethyl azodicarboxylate to give the (*R*)-1-methylheptyl derivatives (Scheme 1b). The β-diketones were prepared by the reaction of the 4-substituted acetophenone with the 4-substituted methyl benzoate and sodium hydride according to the literature procedure (Scheme 1c),[8] followed by formation of the thallium salts by reaction with thallium ethoxide (Scheme 1d).[9] The mononuclear complexes were prepared by the reaction of the thallium β-diketonates with the appropriate chloro-bridged dimer.[6]

Mesogenic Properties: The transition temperatures of the twelve complexes are given in Table 1. It can be seen that as the number of chiral carbons increases, the transition temperatures decrease. The parent complex (**1**), which contains four achiral decyloxy chains, clears at 155 °C, whereas complexes which contain one chiral chain (**2**, **3** and **4**) all have clearing points that are about 40 °C lower, regardless of the position of the chiral chain. It is remarkable that when the chiral group is in the imine ligand (compounds **2** and **3**) only monotropic behaviour is observed. On the other hand, compound **4**, bearing the chiral group in the β-diketone, exhibits enantrotropic mesophases over a wide temperature range (52 °C). This phenomenon can be understood by taking into account the asymmetric geometry of these complexes. A detailed explanation of this point is given in the section on ferroelectric properties of the pure compounds (see below). The introduction of the second chiral carbon leads to further reduction in the mesogenic properties, which are monotropic in all cases (compounds **5**, **6** and **7**), or to complete loss of liquid crystallinity (compound **8**). Compounds that contain three or more chiral carbons are, without exception, not liquid crystalline; indeed, most (compounds **9**, **10** and **12**) are viscous oils which only change viscosity with temperature.

Table 1. Transition temperatures of the complexes **1**–**12** shown in Figure 2 (C_8^* = (*R*)-2-methylheptyl, C_{10} = decyl).

	R^1	R^2	R^3	R^4	Transition temperatures (°C) [a]
1	C_{10}	C_{10}	C_{10}	C_{10}	K 80 S_C 150 S_A 154 N 155 I
2 [b]	C_8^*	C_{10}	C_{10}	C_{10}	K 118 (S_C^* 109 S_A 117) I
3	C_{10}	C_8^*	C_{10}	C_{10}	K 118 (S_C^* 114) I
4 [c]	C_{10}	C_{10}	C_8^*	C_{10}	K 63 S_C^* 104 Ch 115 I
5	C_8^*	C_8^*	C_{10}	C_{10}	K 72 (S_C^* 60) I
6 [c]	C_8^*	C_{10}	C_8^*	C_{10}	K 85 (S_A 77) I
7 [c]	C_{10}	C_8^*	C_8^*	C_{10}	K 93 (S_Y 60 S_X 64) [d] I
8	C_{10}	C_{10}	C_8^*	C_8^*	K 67 I
9 [c]	C_8^*	C_8^*	C_8^*	C_{10}	viscous oil
10	C_8^*	C_{10}	C_8^*	C_8^*	viscous oil
11	C_{10}	C_8^*	C_8^*	C_8^*	K 77 I
12	C_8^*	C_8^*	C_8^*	C_8^*	viscous oil

[a] Phases: K = crystalline, S_C = smectic C, S_A = smectic A, N = nematic, I = isotropic, S_C^* = chiral smectic C, Ch = cholesteric; notation: A *T* B indicates that the phase transition A–B takes place at temperature *T*. [b] (*S*) isomer of this compound previously reported in ref. [4]. [c] Mixture of (*E*) and (*Z*) isomers. [d] S_X, S_Y = unidentified monotropic ordered smectic phases; S_X = orthogonal (probably S_B), S_Y = tilted (probably S_I or S_F).

Mesophase Characterisation: Cholesteric, smectic A and smectic C phases were assigned on the basis of their optical textures[10] and confirmed by X-ray diffraction studies. The cholesteric phase was identified by the "oily streak" texture. The characteristic focal-conic and homeotropic textures of the smectic A phase were clearly identified in the cooling process. The chiral smectic C phases showed *schlieren* and broken focal-conic textures; no dechiralisation lines were observed. When the samples showing this S_C^* phase were submitted to mechanical stress a "pseudo-homeotropic" texture appeared. In compound **7** two ordered smectic mesophases were detected. The mesophase that appeared at higher temperature was orthogonal and the second tilted. Because it was impossible to study these phases by X-ray diffraction techniques, we have tentatively assigned the former as S_B (mosaic texture) and the latter as S_I or S_F (schlieren and pseudohomeotropic textures) by using optical microscopy.

Ferroelectric Properties—The Pure Complexes: Unfortunately, only five of the twelve complexes prepared show a smectic C phase, and only four of these examples contain a chiral carbon (compounds **2**, **3**, **4** and **5**). The ferroelectric properties of these four compounds have been studied, and the properties are shown in Table 2. Compound **5** bearing two chiral carbons shows a very viscous monotropic S_C phase. Its ferroelectric properties were consequently measured under different conditions than for the other three compounds (see Experimental Procedure). For this reason this compound is not included in the discussion of the ferroelectric properties of the pure complexes. The temperature dependencies of their spontaneous polarisations (P_s) are shown in Figure 3.

Although all three compounds contain only one chiral carbon, there are marked differences in the magnitude of their

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Table 2. Ferroelectric properties of pure complexes **2–5** with a chiral smectic C phase.

	P_s(max) [a] ($nC\,cm^{-2}$)	$P_s(T_c-10)$ [b] ($nC\,cm^{-2}$)	τ(max) [c] ($ms\,V\,\mu m^{-1}$)	$\tau(T_c-10)$ ($ms\,V\,\mu m^{-1}$)	γ(max) [d] (Pa s)	$\gamma(T_c-10)$ (Pa s)
2	36.8	33.5	2.9	2.0	0.57	0.39
3	27.7	26.5	1.8	1.8	0.28	0.28
4	9.7	9.5	3.0	2.7	0.17	0.14
5		30 [e]		78 [e]		13 [e]

[a] P_s: spontaneous polarisation. [b] T_c: temperature of transition to S_C^* phase in the cooling process. [c] τ: switching time. [d] γ: rotational viscosity. [e] These properties were measured at T_c-7. The high viscosity of the S_C^* phase in compound **4** rendered measurements at lower temperatures impossible.

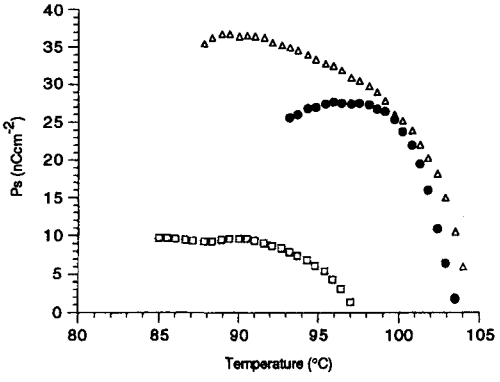

Fig. 3. Temperature dependence of the spontaneous polarisation of compounds **2** (△), **3** (●) and **4** (□).

spontaneous polarisations. The P_s(max) of compound **2** (36.8 $nC\,cm^{-2}$) is higher than that of compound **3** (27.7 $nC\,cm^{-2}$), which, in turn, is significantly higher than that of compound **4** (9.7 $nC\,cm^{-2}$). Similar values of spontaneous polarisation are obtained at (T_c-10) °C. It is clear that the position of the chiral carbon in the core plays an important role in determining the magnitude of P_s, and it is interesting to note that, within this series, the least effective position for the chiral tail is in the β-diketone ligand.

If we consider the structure of the molecule, there are several factors that might explain the low P_s obtained when the chiral carbon is in the diketone ligand. The core of the complex is K-shaped, and both chains R^1 and R^2 in the complex lie along the main molecular axis (shown in Fig. 4), which incorporates the Schiff base ligand and the palladium/Schiff base ring system. The chains R^3 and R^4 would also be expected to lie parallel to the main molecular axis, thus leading to a more "rodlike" shape of the molecule, which can pack more efficiently (a similar effect to that found previously in carboxylato-bridged complexes).[11] However, the rigidity and geometry of the K-shaped aryl core means that the R^3 and R^4 chains, although in a parallel disposition with respect to the molecular axis, are quite remote from R^1 and R^2 and from the metal centre. It is well known from organic systems that the polarisation is greatest when the chiral carbon is close to the central molecular core,[12] as are chains R^1 and R^2 in Figure 4.

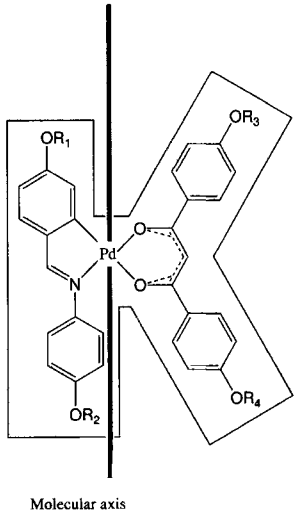

Fig. 4. K-shaped core and main molecular axis of the palladium complex. The structure can be regarded as being made up two rod moieties fused together.

The geometry of the complexes under discussion here is somewhat unusual in comparison to conventional calamitic organic systems. The chiral carbon in the β-diketone moiety, although adjacent to an aromatic ring in each case (R^3 and R^4), is more isolated and remote from the major axis of the molecular core. The remoteness of this chiral carbon in the "secondary" core may lead to less effective coupling of molecular dipoles and thus to relatively low P_s values. Another potentially significant factor in compound **4** (and also compounds **6**, **7** and **9**) is that it consists of a mixture of the (*E*) and (*Z*) isomers, that is, the chiral carbon in the diketone can be in R^3 or R^4 (Fig. 5).[13]

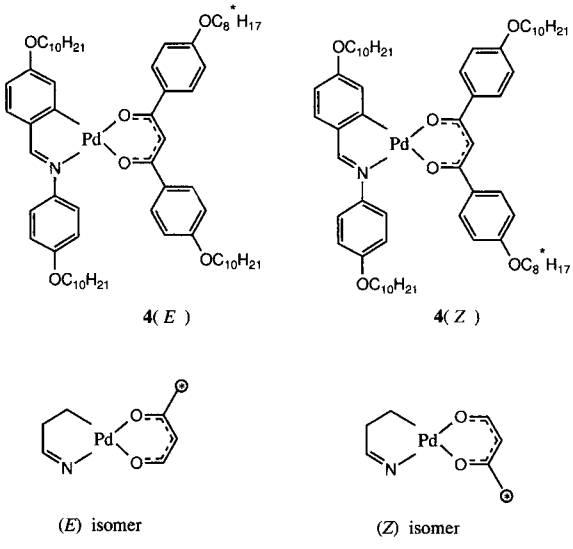

Fig. 5. (*E*) and (*Z*) geometrical isomers of compound **4** (analogous isomerism occurs in compounds **6**, **7** and **9**; priority groups according to the Cahn, Ingold and Prelog system [13]).

However, the two isomers could not be separated, and this influence could not be investigated further. Geometrical factors of this type could also explain the different mesogenic behaviour observed in compounds **2** and **3** compared to compound **4**. When the chiral centre is in the terminal chains of the imine ligand, strong, negative steric factors perturb the molecular interactions; this makes the molecular packing, which is necessary for mesomorphism, difficult. However, when the chiral centre is in the terminal chains of the β-diketone ligand, the negative steric factors are clearly lower, owing to its remoteness from the central rigid core; consequently, enantrotropic behaviour is observed.

Comparison between the P_s values of compounds **2** and **3** shows that the position of the chiral carbon within the Schiff base ligand (R^1 or R^2) also has a marked effect on the spontaneous polarisation: compound **2** has a significantly higher P_s than **3**. This phenomenon can be attributed to the difference in rotational freedom between the aromatic rings that bear the chiral carbon and has been reported previously in dinuclear palladium complexes.[5] It has been well documented that, in order to obtain high P_s values, the coupling of molecular dipoles is an important factor.[12] More effective coupling of the dipoles is obtained when the motion of the chiral carbon is reduced. In the case of compound **3**, it is the anilinic ring that bears the chiral substituent (R^2), and this ring is free to rotate. In com-

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pound **2**, however, the chiral chain (R^1) is in the aldehydic ring which, by virtue of being incorporated in the *ortho*-palladated ring system, is rotationally restricted. Consequently, compound **2** has a higher P_s value than compound **3**. Owing to the unusual geometry of the core unit, compounds **2**, **3** and **4** are, as far as we know, the first series of ferroelectric compounds in which the influence of the chiral group in more than two different positions has been examined.

Ferroelectric Properties—Binary Mixtures: Although the ferroelectric properties of compounds **2**, **3** and **4** could be studied in the pure state, the main aim of the work described here was to perform a comparitive study between all the complexes. The absence of the chiral smectic C phase in a majority of them forced us to consider the study of binary mixtures. Attempts to study binary mixtures of the complexes with commonly used organic hosts, such as 4-hexyloxyphenyl 4-decyloxybenzoate, were unsuccessful due to the limited miscibility of the metal-containing complexes in the structurally different hosts. Fortunately, the achiral mononuclear complex (**1**) shows a smectic C phase with a wide temperature range, and this compound proved to be a suitable host for the study of the other complexes. By trial and error it was found that mixtures containing around 20 mol% of chiral dopant in the host complex were the most suitable for the study of ferroelectric properties. Lower percentage mixtures (10%) led to spontaneous polarisation values that did not differ greatly for different dopants, whereas higher percentage mixtures (30%) proved to be problematic as regards the miscibilty of the dopants containing three or four chiral chains.

Table 3 shows the structures, percentage of the guest component, transition temperatures and ferroelectric properties of the binary mixtures of the complexes in compound **1** in order of increasing P_s values.

Many comparisons between the data are possible, but in order to keep the discussion to a reasonable length, only the most significant trends regarding the ferroelectric property/structure relationships will be highlighted. For the sake of discussion the P_s values will be compared, because the change in tilt angle with temperature was similar for each of the mixtures. Other factors have to be considered when using the P_s(max) values in the comparison because all the curves (plots) of P_s versus temperature in the mixtures show a similar trend, becoming a plateau at lower temperatures (similar to that observed for compound **4** in Fig. 3). Consequently we prefer to use the P_s(max) value, which normally corresponds to the P_s value observed in the plateau.

In general, the spontaneous polarisation values increase as the number of chiral carbons in the molecule increases. The compounds in Table 3 have been subdivided into four groups in order to facilitate the discussion. The first group comprises the complexes that contain only one chiral carbon, and the second, third and fourth groups contain the complexes with two, three and four chiral carbons, respectively. In the discussion which follows the binary mixtures will be indicated by the prefix M. For example, M 2 is the binary mixture of compound **2** in the host compound **1**.

As can be seen, all the mixtures show a smectic A phase above the chiral smectic C phase, and in three mixtures (**M4**, **M7** and **M8**) a cholesteric phase is also observed over a short range. The transition temperature S_A–S_C gradually decreases as the number of chiral carbons in the guest complex increases (group 1 around 135 °C, group 2 around 126 °C, group 3 around 118 °C and group 4 at 114 °C). In all cases the mixtures show a chiral smectic C phase range wider than 20 °C.

If we consider the complexes containing one chiral carbon (group 1 in Table 3), we can see that the trend found in the pure compounds relating the position of the chiral substituent with spontaneous polarisation is again evident in the binary mixtures. Mixture **M4**, containing the chiral carbon in the β-diketone ligand, has a relatively low P_s(max) of 1.7 nC cm^{-2}. In **M3** the chiral carbon is in the anilinic ring (R^2 in Fig. 2), and this mixture shows a P_s(max) of 3.3 nC cm^{-2}, whereas **M2**, with the chiral carbon in the aldehydic ring (R^1, Fig. 2), shows a P_s(max) of 4.8 nC cm^{-2}. A clear order for increasing P_s values is seen: aldehydic ring > anilinic ring > β-diketone. The reasons for this order were discussed above for the pure compounds.

The positional effects discussed above are again evident in mixtures of compounds containing more than one chiral centre, although the effects are often far less marked. Mixture **M8** (group 2) shows the lowest P_s(max) (5.1 nC cm^{-2}) of the compounds containing two chiral centres. Both chiral carbons in this compound are situated in the remote β-diketone unit. A similar conclusion conclusion can be drawn as for the mixtures in group 1 and for the pure compounds: chiral carbons in the diketone core do not give rise to high P_s values. The mixture with the highest P_s(max) value within group 2 is **M5**, which has a P_s(max) of 8.5 nC cm^{-2}. In this case both chiral carbons are situated in the Schiff base core. Mixtures **M6** and **M7** exhibit the same intermediate P_s(max) value of 7.0 nC cm^{-2}. In this case no difference between the compounds with the chiral carbon in the fixed aldehydic ring (**M6**) and in the anilinic ring

Table 3. Structures and properties of ca. 20 mol% binary mixtures of complexes in host compound **1**.

Guest [a]	% Guest	Transition T [c]				P_s(max) [d]	$P_s(T_c-10)$ [e]	P_o [f]	$P_o(T_c-10)$	θ(max) [g]	$\theta(T_c-10)$	τ(max) [h]	$\tau(T_c-10)$	γ(max) [i]	$\gamma(T_c-10)$
		I–S_A	I–Ch	Ch–S_A	S_A–S_C										
4 [b]	19.6		140	138	133	1.7	1.6	3.2	3.2	32	30	3.7	2.9	0.04	0.03
3	20.1	141			136	3.3	2.0	6.8	4.1	29	29	3.9	1.8	0.07	0.02
2	19.9	141			135	4.8	2.6	9.3	5.5	31	28	3.5	1.3	0.09	0.02
8	20.6		138	132	127	5.1	3.0	10.2	6.8	30	26	3.1	1.1	0.09	0.02
7 [b]	20.5		135	132	128	7.0	4.9	15.4	10.8	27	27	3.3	1.8	0.13	0.05
6 [b]	19.4	134			127	7.0	4.9	14.0	10.4	30	28	4.1	1.4	0.17	0.04
5	19.6	131			124	8.5	6.4	17.0	12.8	30	30	3.5	1.5	0.17	0.05
11	20.1	127			120	7.9	7.0	15.8	15.4	30	27	4.2	2.0	0.17	0.08
10	19.8	132			117	8.0	6.9	16.5	16.3	29	25	4.2	1.5	0.17	0.06
9 [b]	20.7	130			120	8.7	7.4	18.1	16.3	29	27	4.2	1.9	0.16	0.08
12	19.6	122			114	12.1	11.0	24.2	24.2	30	27	4.1	1.6	0.25	0.09

[a] For R^1, R^2, R^3 and R^4 refer to Figure 2. [b] Mixture of (*E*) and (*Z*) isomers. [c] Measured in °C during the cooling process in the electrooptical cells. [d] P_s (nC cm^{-2}): spontaneous polarisation. [e] T_c (°C): temperature of transition to S_C^* phase in the cooling process. [f] P_o (nC cm^{-2}): normalised polarisation. [g] θ (°): optical angle. [h] τ (ms V μm^{-1}): switching time. [i] γ (Pa s): rotational viscosity.

(**M7**) was detected. This fact coincides with the existence of (*E*/*Z*) isomers as exhibited by compounds **6** and **7**.

The next group of mixtures to be considered contain complexes with three chiral carbons (**M9**, **M10** and **M11** in group 3, Table 3). Once again no significant difference was found between compounds bearing the chiral carbon in the aldehydic or anilinic ring (**M10** and **M11**, respectively); both show very similar P_s(max) values of around 8 nC cm^{-2}. With two chiral carbons in the Schiff base ligand, **M9** again shows a somewhat higher P_s(max) value of 8.7 nC cm^{-2}; however, in this case the difference is much less significant than that observed in the comparable mixtures of group 2. It is worthy of note that, although compound **5** contains only two chiral carbons, **M5** shows a P_s value similar to those of **M9**, **M10** and **M11**, all of which contain three chiral centres. Indeed, generally speaking, there is only a rather small difference between the P_s values of mixtures from groups 2 and 3 (except for **M8** which, in the absence of a chiral carbon on the Schiff base ligand, shows a smaller polarisation than expected). In other words, the addition of the third chiral carbon in the β-diketone ligand (**M7** → **M11**; **M6** → **M10**; **M5** → **M9**) makes only a very small contribution to the spontaneous polarisation.

In the comparison between groups 1, 2 and 3 a clear trend appears: the differences in P_s values arising from positional differences of the chiral carbons are for more marked in compounds containing one or two chiral centres and become less significant when three chiral centres are introduced.

The trends regarding the influence of the position of chiral centres on the spontaneous polarisation are clear. We will now discuss the effect of adding chiral centres to a system and assess whether their contributions to the polarisation are additive.

The addition of a second chiral centre to compounds already containing one chiral carbon leads to significant increases in th P_s (compare compounds in group 1 and 2). The increases observed are, in all cases, greater than expected from a purely additive contribution of the chiral centres to P_s. The expected values of the P_s(max) (nC cm^{-2}) in compounds of group 2 would to be 3.4 for **M8**, 5.0 for **M7**, 6.5 for **M6** and 8.1 for **M5**, all of these lower than the experimental values. In contrast, the addition of a third chiral centre to any of the complexes containing two chiral carbons only leads to modest increases in P_s (compare groups 2 and 3). The smallest increase of only 0.2 nC cm^{-2} is observed for the addition of a chiral centre to the β-diketone ligand (cf. 8.5 nC cm^{-2} for **M5** with 8.7 nC cm^{-2} for **M9**). In this case, the existence of (*E*/*Z*) isomerism in compound **9** might also play an important role in the observed phenomenon. For mixtures of **12**, which contains four chiral carbons, the trend of diminishing increases in P_s is reversed. Within the series, **M12** shows a remarkably high P_s (12.1 nC cm^{-2}). This trend is comparable to that reported for dinuclear palladium complexes containing four chiral centres and homologues containing fewer chiral centres.[5]

It is clear the contributions of the chiral centres to the overall spontaneous polarisation of the system are not simply additive and that an additional factor must be involved. Compound **12** is indeed a special case in that each of the four terminal positions bears a chiral substituent. In order to explain this phenomenon, we must consider the packing of the molecules and the possible differences in molecular interactions that may occur. This is especially important in systems consisting of complexes with unusual geometries and of much greater width than typical rod-like organic molecules, such as the complexes reported here and previously.[5] These H- or K-shaped molecules show significant restrictions in rotation about the main molecular axis.[14] For this reason the number and positions of the chiral chains is especially relevant in the molecular arrangements.

The K-shaped molecules can, to a rough approximation, be regarded as two fused rods, and we can compare the possible orientations for complexes **5**, **9** and **12** as representative examples. In compound **12** the effect of the positions of the chiral centres on the magnitude of the spontaneous polarisation need not be considered, since all four positions bear a chiral centre. Consequently, in contrast to compounds containing achiral chains, adjacent molecules of **12** in any relative orientation lead to chiral centres coming into close proximity (Fig. 6a). This would be expected to lead to a significantly higher density of interactions between chiral centres and enhanced spontaneous polarisation, which is indeed observed.

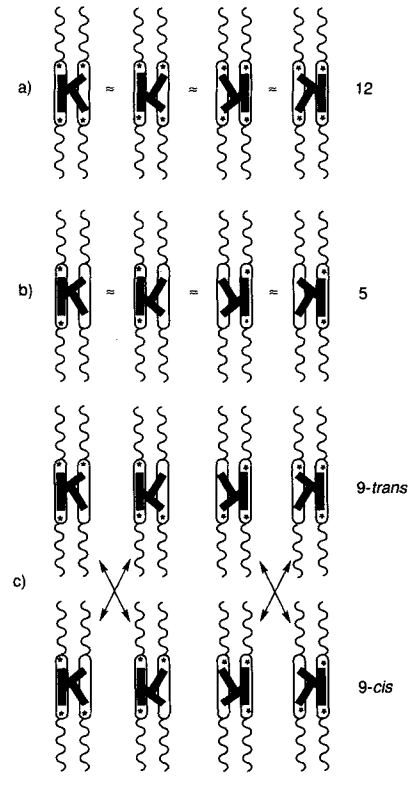

Fig. 6. Schematic representation of the molecules as two fused rods (the asterisks denote chiral carbons) showing the relative molecular orientations of a) complex **12** in the S_C layer, b) complex **5** and c) complex **9**, which is a mixture of (*E*) and (*Z*) isomers.

Complex **5** has two chiral carbons in the imine ligand and behaves in a similar way to complex **12**, but with a clearly lower degree of interaction between the chiral carbons (Figure 6b). Finally, complex **9** with three chiral carbons has a greater number of possible molecular orientations in mixtures (Fig. 6c), owing to the presence of (*E*) and (*Z*) isomers. This would be expected to lead to a less effective dipolar coupling in the ferroelectric phase. Consequently, the introduction of the third chiral carbon does not significantly increase the P_s value in relation to **M5**.

Response Times (τ) and Rotational Viscosities (γ): The rotational viscosities and response times of the pure compounds are given in Table 2 and those of the mixtures in Table 3. The response times are in the order of 2–3 ms in the pure compounds and 3–4 ms in the mixtures. Although these values are not high

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compared to those of organic low molecular weight ferroelectric systems, they are similar to those observed in ferroelectric polymers and in classical nematic devices.[15]

As far as the rotational viscosities of the complexes are concerned, the main trend observed is that the viscosity increases as the number of chiral chains increases. The rotational viscosities range from 0.04 Pa s in mixture **4** (one chiral carbon in the diketone) to 0.25 Pa s in mixture **12** (four chiral chains). The rotational viscosities observed in the mixtures are far higher than those observed in rodlike organic ferroelectric systems. The high viscosity values are not surprising, given the unusual K-shaped structure of both guest and host in the mixtures, and are probably a consequence of the hindered or cooperative rotation necessary during the switching of noncylindrical molecules.

Conclusions

The main conclusions that can be drawn from the results presented here concern the relative effectiveness of the position of the chiral carbons in contributing to the overall P_s of the system. These conclusions are best illustrated by the compounds containing one chiral centre, and the trends observed in both pure complexes and binary mixtures are the same. Chiral carbons in the main linear molecular core (R^1 and R^2 in the Schiff base) contribute more effectively to the spontaneous polarisation. In addition, the chiral group in the rotationally restricted aldehydic ring is more effective in promoting higher P_s values than that in the rotationally free anilinic ring. Chiral carbons in the more remote β-diketone moiety contribute less to the overall P_s. The influence of the positions of chiral centres on P_s is also apparent in compounds containing more than one chiral centre, although it becomes less marked as the number of chiral centres increases.

The number of chiral carbons present in each system also has an influence on the spontaneous polarisation. In general, P_s increases with the number of chiral centres present. The addition of a second chiral centre leads to comparatively large increases in P_s. The relative magnitudes of the increases in P_s observed are commensurate with the position of the chiral centre introduced. The addition of a third chiral centre, although causing an increase in the P_s, does not have such a marked effect as the change from one chiral centre to two. Indeed, the influence of both the number and position of the chiral centres appears to be less distinct in compounds containing three chiral centres than in their analogues with fewer chiral centres. The existence of (*E*/*Z*) isomers in some compounds has also been shown to have a negative influence on ferroelectric properties, leading to a decrease in P_s values.

The compound containing four chiral centres is an exception, and shows a higher P_s than expected given the trends discussed above. This is thought to be due to packing arrangements which lead to favourable interactions between molecular dipoles.

Experimental Procedure

Materials: Owing to the repetitive nature of the synthesis of the complexes and their structural similarity, the synthesis of one representative example is described. The analytical and spectroscopic data of the rest of the final compounds are given below.

Synthesis and characterisation of 1: To a stirred solution of the chloro-bridged complex (0.78 g, 0.6 mmol) in dry dichloromethane (8 mL) was added a suspension of the thallium β-diketonate (0.91 g, 1.2 mmol) in dry dichloromethane (10 mL). The mixture was stirred at room temperature for 1 h, filtered, and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica gel, dichloromethane:hexane, 1:1) followed by crystallisation (ethanol/methyl ethyl ketone) to give a yellow solid (several complexes did not crystallise from solution and were purified by column chromatography only). Yield: 1.2 g, 87%. Analysis calculated (found): C 72.05 (71.97), H 9.12 (8.97), N 1.20 (1.23); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.85 (m, 12H), 1.20–1.60 (m, 56H), 1.70–1.70 (m, 8H), 3.95–4.10 (m, 6H), 4.12 (t, 2H), 6.60 (s, 1H), 6.61 (dd, 1H), 6.79 (d, 2H), 6.89 (d, 2H), 6.92 (d, 2H), 7.28 (d, 1H), 7.33 (d, 1H), 7.71 (d, 2H), 7.96 (d, 2H), 7.99 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1604 (C=N), 1588 (C=O), 1541 (C=C), 1251 (C–O).

Compound 2: yield 80%. Analysis calculated (found): C 71.61 (71.62), H 9.06 (8.83), N 1.23 (1.27); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.85 (m, 12H), 1.20–1.60 (m, 53H), 1.70–1.90 (m, 8H), 3.95–4.10 (m, 6H), 4.60 (m, 1H), 6.61 (s, 1H), 6.60 (dd, 1H), 6.79 (d, 2H), 6.90 (d, 2H), 6.94 (d, 2H), 7.29 (d, 1H), 7.31 (d, 1H), 7.42 (d, 2H), 7.71 (d, 2H), 7.97 (d, 2H), 7.99 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1604 (C=N), 1586 (C=O), 1537 (C=C), 1251 (C–O).

Compound 3: yield 67%. Analysis calculated (found): C 71.52 (71.62), H 9.36 (8.83), N 1.13 (1.27); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.85 (m, 12H), 1.20–1.50 (m, 53H), 1.70–1.90 (m, 8H), 3.95 (t, 2H), 3.99 (t 2H), 4.12 (t, 2H), 4.38 (m, 1H), 6.61 (s, 1H), 6.62 (dd, 1H), 6.78 (d, 2H), 6.88 (d, 2H), 6.92 (d, 2H), 7.30 (d, 1H), 7.33 (d, 1H), 7.42 (d, 2H), 7.71 (d, 2H), 7.97 (d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1601 (C=N), 1586 (C=O), 1536 (C=C), 1252 (C–O).

Compound 4: yield 56%. Analysis calculated (found): C 71.63 (71.62), H 9.19 (8.83), N 1.21 (1.27); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.85 (m, 12H), 1.20–1.70 (m, 53H), 1.70–1.90 (m, 8H), 3.98 (m, 4H), 4.12 (t, 2H), 4.40 (m, 1H), 6.60 (s, 1H), 6.62 (dd, 1H), 6.78 (m, 2H), 6.90 (m, 2H), 6.94 (d, 2H), 7.29 (d, 1H), 7.32 (d, 1H), 7.43 (d, 2H), 7.70 (d, 2H), 7.98 (d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1603 (C=N), 1586 (C=O), 1538 (C=C), 1251 (C–O).

Compound 5: yield 77%. Analysis calculated (found): C 71.50 (71.26), H 8.85 (8.68), N 1.07 (1.30); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80–0.85 (m, 12H), 1.20–1.70 (m, 52H), 1.70–1.80 (m, 6H), 3.95 (t, 2H), 4.00 (t 2H), 4.39 (m, 1H), 4.60 (m, 1H), 6.60 (d, 1H), 6.61 (s, 1H), 6.78 (d, 2H), 6.89 (d, 2H), 6.92 (d, 2H), 7.26–7.34 (m, 2H), 7.42 (d, 2H), 7.72 (d, 2H), 7.98 (d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1602 (C=N), 1577 (C=O), 1541 (C=C), 1248 (C–O).

Compound 6: yield 64%. Analysis calculated (found): C 71.37 (71.26), H 8.43 (8.68), N 1.24 (1.30); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.90 (m, 12H), 1.20–1.70 (m, 52H), 1.70–1.80 (m, 6H), 3.95–4.05 (m, 4H), 4.40 (m, 1H), 4.58 (m, 1H), 6.60–6.64 (m, 2H), 6.78 (2d, 2H), 6.88 (2d, 2H), 6.93 (d, 2H), 7.29 (d, 1H), 7.31 (s, 1H), 7.42 (d, 2H), 7.72 (2d, 2H), 7.96 (2d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1604 (C=N), 1586 (C=O), 1537 (C=C), 1250 (C–O).

Compound 7: yield 61%. Analysis calculated (found): C 71.35 (71.26), H 8.87 (8.68), N 1.25 (1.30); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.89 (m, 12H), 1.20–1.60 (m, 50H), 1.60–1.90 (m, 8H), 4.00 (t, 2H), 4.13 (t, 2H), 4.30–4.50 (m, 2H), 6.61 (s, 1H), 6.63 (dd, 1H), 6.76 (2d, 2H), 6.89 (d, 2H), 6.93 (d, 2H), 7.30 (d, 1H), 7.33 (d, 1H), 7.42 (d, 2H), 7.71 (d, 2H), 7.97 (d, 2H), 8.01 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1604 (C=N), 1586 (C=O), 1537 (C=C), 1253 (C–O).

Compound 8: yield 40%. Analysis calculated (found): C 71.25 (71.26), H 9.09 (8.68), N 1.26 (1.30); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.89 (m, 12H), 1.20–1.70 (m, 50H), 1.70–1.90 (m, 8H), 3.99 (t, 2H), 4.12 (t, 2H), 4.35–4.45 (m, 2H), 6.60 (s, 1H), 6.62 (dd, 1H), 6.79 (d, 2H), 6.88 (d, 2H), 6.94 (d, 2H), 7.30 (d, 1H), 7.32 (d, 1H), 7.42 (d, 2H), 7.70 (d, 2H), 7.98 (d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1601 (C=N), 1586 (C=O), 1537 (C=C), 1250 (C–O).

Compound 9: yield 54%. Analysis calculated (found): C 70.97 (70.87), H 9.01 (8.53), N 1.22 (1.33); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.89 (m, 12H), 1.20–1.70 (m, 49H), 1.70–1.90 (m, 6H), 3.95–4.05 (m, 2H), 4.30–4.50 (m, 2H), 4.60 (m, 1H), 6.58–6.65 (m, 2H), 6.76 (2d, 2H), 6.85–7.00 (m, 4H), 7.25–7.35 (m, 2H), 7.42 (d, 2H), 7.72 (2d, 2H), 7.85–7.95 (m, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1603 (C=N), 1576 (C=O), 1538 (C=C), 1250 (C–O).

Compound 10: yield 54%. Analysis calculated (found): C 71.94 (70.87), H 8.79 (8.53), N 1.24 (1.33); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–0.87 (m, 12H), 1.20–1.60 (m, 49H), 1.79 (m, 6H), 4.00 (t, 2H), 4.41 (m, 2H), 4.59 (m, 1H), 6.55–6.65 (m, 2H), 6.78 (d, 2H), 6.88 (d, 2H), 6.94 (d, 2H), 7.25–7.35 (m, 2H), 7.42 (d, 2H), 7.71 (d, 2H), 7.96 (d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1602 (C=N), 1576 (C=O), 1538 (C=C), 1250 (C–O).

Compound 11: yield 35%. Analysis calculated (found): C 71.12 (70.87), H 8.95 (8.53), N 1.28 (1.33); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82–0.88 (m, 12H), 1.20–1.70 (m, 49H), 1.80 (m, 6H), 4.12 (t, 2H), 4.34–4.44 (m, 3H), 6.61 (s, 1H), 6.63 (dd, 1H), 6.76 (d, 2H), 6.88 (d, 2H), 6.93 (d, 2H), 7.30 (d, 1H), 7.33 (d, 1H), 7.42 (d, 2H), 7.71 (d, 2H), 7.96 (d, 2H), 8.01 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1600 (C=N), 1586 (C=O), 1531 (C=C), 1247 (C–O).

Compound 12: yield 51%. Analysis calculated (found): C 70.16 (70.47), H 7.90 (8.37), N 1.27 (1.37); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82–0.92 (m, 12H), 1.20–1.70 (m, 48H), 1.70–1.90 (m, 4H), 4.35–4.45 (m, 3H), 4.56–4.64 (m, 1H), 6.55–6.65 (m, 2H), 6.75 (d, 2H), 6.90 (d, 2H), 6.94 (d, 2H), 7.25–7.35 (m, 2H), 7.42 (d, 2H), 7.70 (d, 2H), 7.97 (d, 2H), 8.00 (s, 1H); IR (Nujol): $\tilde{\nu}$ (cm^{-1}) = 1601 (C=N), 1580 (C=O), 1537 (C=C), 1251 (C–O).

Techniques: Microanalysis was performed with a Perkin-Elmer 240-B microanalyser. Infrared spectra were recorded on a Pekin-Elmer 1600 (series FTIR) Spectrometer in the 400–4000 cm^{-1} spectral range. ^{1}H NMR were recorded on a Varian Unity 300 spectrometer operating at 300 MHz for ^{1}H.

The transition temperatures and the natures of the phases were determined by polarising optical microscopy with an Olympus BH2 microscope with a Mettler FP-82 heating stage and temperature control unit. Transition temperatures were measured by differential scanning calorimetry on a Perkin-Elmer DCS-7 calorimeter calibrated with indium (156.6 °C) and tin (232.1 °C) and with scanning rates of 10 °C per minute.

Powder X-ray diffraction patterns were obtained on a Guinier diffractometer (Huber 644) operating with a Cu($K\alpha_1$) beam issued from a germanium monochromator. The samples were held in rotating Lindemann glass capillaries (0.7 mm o.d.) and heated with a variable-temperature attachment. The diffraction patterns were registered with a scintillation counter.

Spontaneous polarisation, switching times and rotational viscosities of the complexes and binary mixtures were determined simultaneously by the triangular wave method [16,17] by using 4 μm polyimide coated cells with indium tin oxide electrodes (Standish LCD). Electrical fields of 30 V (peak to peak) with a frequency of 50 Hz were applied to samples of both pure complexes and binary mixtures with the exception of the pure compound **7** (100 V, 5 Hz). Tilt angles were determined by the field-reversal method, by observation of the extinction condition. The sign of P_s was determined by rotation of the stage in accordance with Lagerwall's convention [18]. The binary mixtures of the chiral complexes with the achiral host (compound **1**) were prepared by weighing the appropriate amounts of each component and mixing with stirring in the isotopic phase for 1 min. The mixture was then allowed to cool. This operation was repeated twice.

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