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The synthesis of laterally fluorinated alkoxy stilbazoles and some of their mesogenic complexes with Ir(I). The molecular structure of *trans*-4-undecyloxy-3-fluoro-4'-stilbazole

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The synthesis of laterally fluorinated alkoxy stilbazoles and some of their mesogenic complexes with Ir(I). The molecular structure of *trans*-4-undecyloxy-3-fluoro-4'-stilbazole

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A series of 3-fluorinated 4-alkoxy stilbazoles (*n*-3F-OPhVPy) and some of the related 2-fluorinated derivatives (*n*-2F-OPhVPy) have been synthesized; unlike their non-fluorinated counterparts, these new stilbazoles are non-mesomorphic. A single crystal structure determination of 3-fluoro-4-undecyloxy-4'-stilbazole shows the molecule to be planar, *trans* with respect to the double bond and to crystallize in only one of two possible extreme rotational conformers. Reaction of these fluorinated stilbazoles with $[\text{IrCl}(\text{COD})]_2$ under CO affords the complexes *cis*- $[\text{IrCl}(\text{CO})_2(n\text{-XF-OPhVPY})]$ which are non-mesomorphic for $X=3$, but have monotropic phases for $X=2$.

1. Introduction

The lateral fluorination of organic mesogens has been a useful strategy for modifying mesomorphism and subsequently improving the phase characteristics of materials with device potential [1]. The success of this approach has relied on the fact that while fluorine is quite similar in size to hydrogen when bound to an aromatic unit, it can change the polarity of the molecules, affecting intermolecular interactions and hence mesomorphism.

Broadly speaking, the effects of lateral substitution are twofold: a size effect and a dipolar effect. Thus, a lateral group will almost inevitably broaden a molecule and while this may act to promote the nematic phase range [1], it will also lead to a general reduction in clearing temperature (and often melting point). Broadening can also lead to the promotion of the nematic phase range at the expense of an orthogonal smectic phase; this is attributed to the reduction in inter-molecular attractions and the small effect that this has on the nematic phase, which is lower in density than the smectic phases. However, increased lateral dipolar associations can compete with this sterically-induced reduction in intermolecular attraction and promote smectic phases [1].

The position of lateral substitution is also important. For example, fluoro-substitution *ortho* to the cyano group in the ester (**A**) shown in figure 1 lowers both the melting point and clearing point by around 32°C, while *meta*-substitution lowers the melting point by around 50°C, but leaves the clearing point unchanged [1(a)]. However, this can be contrasted with the situation in the relatively non-polar phenyl benzoates (see figure 1, **B**) where fluoro-substitution at either position *X*, *Y* or *Z* lowers the clearing point by around 20°C. Thus, the effect of lateral substitution is found to

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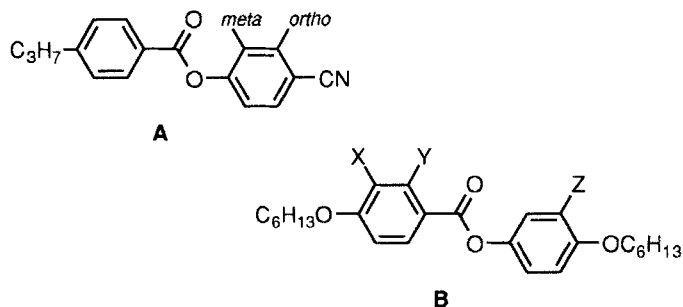


Figure 1.

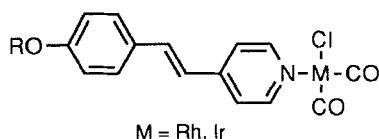


Figure 2. Parent complexes for this study.

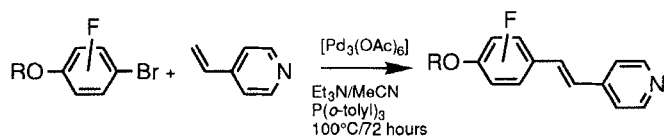
vary between systems. However, few studies of the lateral substitution of mesogenic metal complexes have been reported in the literature [2].

We have recently reported the synthesis, mesomorphism [3] and physical properties [4, 5, 6] of some mesogenic materials formed by complexing 4-alkoxy-stilbazoles to Rh(I) and Ir(I) (see figure 2). We found that for shorter alkoxy chain lengths ($R = C_4H_9O-$ to $C_8H_{17}O-$), the materials showed a nematic phase, while at slightly longer chain lengths ($R = C_7H_{15}O-$ to $C_{17}H_{25}O-$), a S_A phase was seen. Melting points for the materials were typically around 80–90°C, while clearing points were in the range 130–140°C. Given that one of the more general effects of lateral substitution is to destabilize the crystal phase, there was every possibility that fluorinating the stilbazole ligands would result in materials which melted much lower to form mesophases. Further, the mesomorphic range in these materials ($\approx 40^\circ\text{C}$) was probably sufficiently wide so that destabilization of the highest temperature phase would still leave materials with enantiotropic phases. We therefore undertook the synthesis of some 4-alkoxy-3-fluoro-4'-stilbazoles (n -3F-OPhVPy) and some 4-alkoxy-2-fluoro-4'-stilbazoles (n -2F-OPhVPy), which we subsequently complexed to Ir(I). We now report the results of this study.

2. Experimental

2.1. Synthesis

The materials were synthesized according to Scheme 1. Thus, 4-alkoxy-3-fluorobromobenzenes and 4-alkoxy-2-fluorobromobenzenes were prepared from 4-bromo-2-fluorophenol and 4-bromo-3-fluorophenol respectively by standard



Scheme 1. Synthetic scheme for the fluorinated stilbazoles.

Williamson ether procedures. These materials were then coupled with 4-vinylpyridine in a palladium-catalysed Heck reaction [7] to give the related stilbazoles. The procedure was essentially the same as that which we reported for the unsubstituted stilbazoles [8] except that in this Heck reaction, the coupling of aromatic bromides requires the use of $P(o\text{-tolyl})_3$ as a co-catalyst. For the 4-alkoxy-3-fluoro-4'-stilbazoles, the yields were slightly lower than those obtained for the simple stilbazoles, while for the 2-fluoro isomers, yields were much lower. The low yields for the 2-fluoro isomers were a little surprising and were possibly due to steric crowding around the Pd centre during the reaction; attempts are underway to optimize the yields from this coupling.

The iridium complexes were synthesized as previously described [3] and their analytical data are collected in table 1. Briefly, this procedure requires the reaction of $[\text{Ir}(\mu\text{-Cl})(\eta\text{-COD})]_2$ (COD = 1,5-cyclo-octadiene) with two equivalents of stilbazole in dichloromethane at room temperature for 30 min under an atmosphere of CO, followed by precipitation of the product by the addition of hexane. No further purification of the samples was necessary. Dichloromethane was neutralized with potassium carbonate prior to use. 4-Bromo-2-fluorophenol was purchased from Fluorochem, while 4-bromo-3-fluorophenol was the generous gift of Merck Ltd. Elemental analyses were determined by the University of Sheffield Microanalysis Service and NMR spectra were recorded on a Bruker AM250 spectrometer. ^{19}F NMR spectra were referenced to CFCl_3 at 0δ . Analysis by hot-stage optical microscopy was carried out using a Zeiss Labpol microscope equipped with a link-Am TH600 hot-stage, PR600 controller and CS196 cooling accessory.

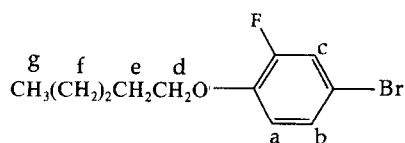
The mixtures used in the phase diagram were prepared by dissolution of the appropriate weights of each compound in dichloromethane in an inert atmosphere, followed by the removal of the solvent. Transition temperatures were recorded on both the first and second heating cycle and good agreement was found between the two, showing solution mixing to be adequate for these studies.

2.2. Preparation of 3-fluorinated stilbazoles

2.2.1. Synthesis of 4-pentoxy-3-fluorobromobenzene

A mixture of 1-bromopentane (3.95 g, 26.2 mmol), 2-fluoro-4-bromophenol (5 g, 26.2 mmol) and potassium carbonate (4 g, 29 mmol) was heated at reflux in acetone (100 cm^3) for 16 h. The reaction mixture was then allowed to cool and water was added to dissolve the potassium bromide produced and any remaining potassium carbonate. The product was then extracted into ether ($3 \times 15\text{ cm}^3$) and the combined organic layers were washed with aqueous sodium chloride (saturated, 15 cm^3) and sodium hydroxide (10 per cent, 15 cm^3). The organic layer was then dried over magnesium sulphate, filtered and the ether removed *in vacuo*. The remaining oil was then vacuum distilled ($80^\circ\text{C}/0.01\text{ mmHg}$) to give 4.07 g (60 per cent yield) of the pure 4-alkoxy-3-fluorobromobenzene.

^1H NMR data



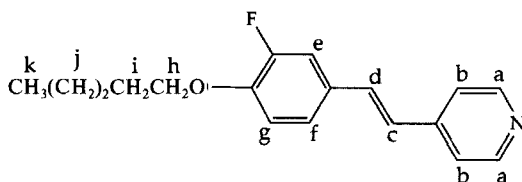
This was treated as an AMNX system.

H_c : $\delta 7.22$ (1 H, $J_{bc} = 2\text{ Hz}$, $J_{ac} \sim 0\text{ Hz}$, $J_{cF} = 10.5\text{ Hz}$); H_b : $\delta 7.17$ (1 H, $J_{bc} = 2\text{ Hz}$, $J_{ab} = 8.5\text{ Hz}$, $J_{bF} = 1.5\text{ Hz}$); H_a : $\delta 6.80$ (1 H, $J_{ac} \sim 0\text{ Hz}$, $J_{ab} = 8.5\text{ Hz}$, $J_{aF} = 9\text{ Hz}$); H_d : $\delta 3.99$ (t, 2 H, $J = 6.7\text{ Hz}$); H_e : $\delta 1.8$ (m, 2 H); H_f : $\delta 1.4$ (m, 4 H); H_g : $\delta 1.8$ (t, 3 H, $J = 7\text{ Hz}$).

2.2.2. Synthesis of 4-pentoxy-3-fluoro-4'-stilbazole

4-Pentoxy-3-fluorobromobenzene (4 g, 15.3 mmol) was placed in a thick-walled pyrex Fischer-Porter tube flushed with argon, together with 4-vinylpyridine (1.8 g, 17.1 mmol), triethylamine (1.55 g, 15.3 mmol) and acetonitrile (10 cm³). The tube was then flushed with argon again and palladium acetate (70 mg, 0.15 mmol) and tri(*o*-tolyl)phosphine (35 mg, 0.15 mmol) were added. The tube was again flushed with argon and the mixture was heated for 72 h at 100°C at constant volume. After the mixture was allowed to cool, the product was extracted with dichloromethane (3 × 15 cm³) and the extract then washed with water (3 × 5 cm³). The layers were separated and the aqueous layer was shaken with more dichloromethane (3 × 15 cm³). The organic layer was dried over magnesium sulphate, filtered and the dichloromethane removed by evaporation. The remaining solid was then extracted (Soxhlet apparatus) with hexane. After removing the hexane, a coloured solid was obtained which was crystallized from acetone to give an off-white solid of analytical purity (3.2 g, 73 per cent). C 75.8 (75.8), H 7.1 (6.9), N 4.9 (4.8).

¹H NMR data

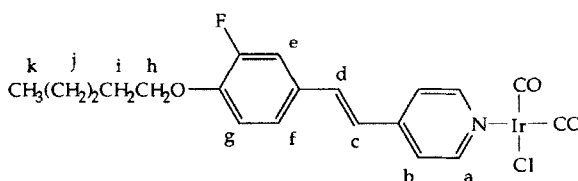


The pyridyl ring was analysed as an AA'XX' system and the fluorinated ring as an AMNX system.

H_a: δ8.58 (2H, *J*_{ab} = 6 Hz, *J*_{aa'} = 1 Hz, *J*_{ab'} ~ 0 Hz); H_b: δ7.33 (2H, *J*_{ba} = 6 Hz, *J*_{bb'} = 2 Hz, *J*_{ba'} ~ 0 Hz); H_c: δ6.86 (1H, *J* = 16 Hz); H_d: δ7.19 (1H, *J* = 16 Hz); H_e: δ7.29 (1H); H_f: δ7.20 (1H) peaks are not resolved. H_g: δ6.95 (1H, *J*_{gf} = 8.5 Hz, *J*_{gF} = 8.5 Hz, *J*_{ge} ~ 0 Hz); H_h: δ4.05 (t, 2H, *J* = 7 Hz); H_i: δ1.85 (m, 2H); H_j: δ1.43 (m, 4H); H_k: δ0.94 (t, 3H, *J* = 8 Hz). ¹⁹F{¹H} NMR: δ - 134 (s).

2.2.3. Ir(I) complex

¹H NMR data



The pyridyl ring was analysed as an AA'XX' system and the fluorinated ring as an AMNX system.

H_a: δ8.65 (2H, *J*_{ab} = 6 Hz, *J*_{aa'} = 1 Hz, *J*_{ab'} ~ 0 Hz); H_b: δ7.50 (2H, *J*_{ba} = 6 Hz, *J*_{bb'} = 2 Hz, *J*_{ba'} ~ 0 Hz); H_c: δ6.87 (1H, *J* = 16 Hz); H_d: δ7.29 (1H, *J* = 16 Hz); H_e: δ7.34 (1H peak not resolved); H_f: δ7.26 (1H peak not resolved); H_g: δ6.97 (1H, *J*_{gf} = 8 Hz, *J*_{gF} = 8 Hz, *J*_{ge} ~ 0 Hz); H_h: δ4.07 (t, 2H, *J* = 7 Hz); H_i: δ1.84 (qn, 2H); H_j: δ1.42 (m, 4H); H_k: δ0.94 (t, 3H, *J* = 8 Hz). (¹⁹F{¹H} NMR: δ - 134 (s)).

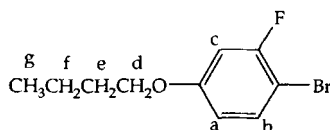
Other 3-fluorinated stilbazoles were prepared using the same route and their yields and analysis data are shown in table 2. That the vinylic group has a *trans*-disposition is shown by *J*_{HcHd} = 16 Hz.

2.3. Preparation of 2-fluorinated stilbazoles

The isomeric 2-fluorinated stilbazoles were made in a similar way, although in general, the yields were somewhat lower and the materials were more difficult to purify.

2.3.1. 4-Butoxy-2-fluorobromobenzene

A mixture of 1-bromobutane (1.43 g, 10.5 mmol), 3-fluoro-4-bromophenol (2.0 g, 10.5 mmol) and potassium carbonate 2 g (14.3 mmol) was heated at reflux in acetone (12 cm³) for 16 h. The reaction mixture was allowed to cool and water was added to dissolve the potassium bromide produced and any remaining potassium carbonate. The mixture was shaken with ether (3 × 5 cm³) and the combined organic layers were washed with aqueous sodium chloride (saturated, 5 cm³) and sodium hydroxide (10 per cent, 5 cm³). The organic layer was then dried over magnesium sulphate, filtered and the ether removed *in vacuo*. The remaining oil was then vacuum distilled (65°C/0.01 mmHg) to give 1.87 g (72 per cent yield) of the pure 4-butoxy-2-fluorobromobenzene.

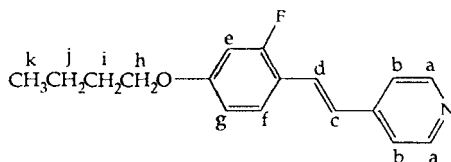
¹H NMR data

This was treated as an AMNX system.

H_c: δ6.68 (1 H, J_{bc} = 0 Hz, J_{ac} = 3 Hz, J_{cF} = 10 Hz); H_b: δ7.39 (1 H, J_{bc} = 0 Hz, J_{ab} = 9 Hz, J_{bF} = 9 Hz); H_a: δ6.60 (1 H, J_{ac} = 3 Hz, J_{ab} = 9 Hz, J_{aF} = 1 Hz); H_d: δ3.92 (t, 2 H, J = 6.5 Hz); H_e: δ1.76 (m, 2 H); H_f: δ1.48 (m, 2 H); H_g: δ1.8 (t, 3 H, J = 7 Hz).

2.3.2. Synthesis of 4-butoxy-2-fluoro-4'-stilbazole

The 4-butoxy-2-fluorobromobenzene (1.85 g, 7.5 mmol) was placed in a thick-walled pyrex Fischer-Porter tube flushed with argon, together with 4-vinylpyridine (0.88 g, 8.4 mmol), triethylamine 0.76 g, 7.5 mmol and acetonitrile (3.5 cm³). The tube was then flushed with argon again and palladium acetate (34 mg, 0.06 mmol) and tri(*o*-tolyl)phosphine (17 mg, 0.06 mmol) were added. The tube was again flushed with argon and the mixture was then heated for 72 h at 100°C at constant volume. On cooling, the product was extracted into dichloromethane (3 × 5 cm³) which was then washed with water (3 × 5 cm³). The layers were separated and the aqueous layer was shaken with more dichloromethane (3 × 5 cm³). The organic layer was dried over magnesium sulphate and filtered. The dichloromethane was then removed by distillation. The remaining liquor was triturated with cold pentane and the solid obtained was filtered and subsequently extracted repeatedly (Soxhlet apparatus) with pentane. After removing the pentane, the product was crystallized from hot petroleum ether (40/60) and an off-white solid of analytical purity was obtained (0.74 g, 36 per cent). C 75.3 (75.5), H 6.7 (7.0), N 5.2 (5.1).

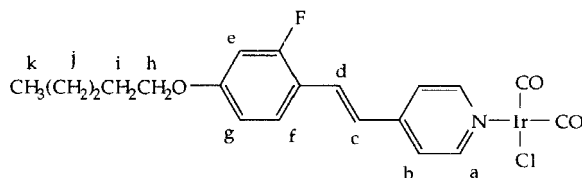
¹H NMR data

The pyridyl ring was analysed as an AA'XX' system and the fluorinated ring as an AMNX system.

H_a: δ8.56 (2H, $J_{ab}=6$ Hz, $J_{aa'}=1$ Hz, $J_{ab'}\sim 0$ Hz); H_b: δ7.36 (2H, $J_{ba}=6$ Hz, $J_{bb'}=2$ Hz, $J_{ba'}\sim 0$ Hz); H_c: δ7.39 (1H, $I=16$ Hz); H_d: δ6.95 (1H, $J=16$ Hz); H_e: δ7.51 (1H, $J_{eF}=9$ Hz, $J_{cg}=0$ Hz, $J_{ef}=9$ Hz); H_f: δ6.72 (1H, $J_{fg}=2.5$ Hz, $J_{fe}=9$ Hz, $J_{fF}\sim 0$ Hz); H_g: δ6.64 (1H, $J_{gf}=2.5$ Hz, $J_{gF}=12$ Hz, $J_{ge}\sim 0$ Hz); H_h: δ3.96 (t, 2H, $J=6.5$ Hz); H_i: δ1.80 (m, 2H); H_j: δ1.45, (m, 2H); H_k: δ0.94 (t, 3H, $J=7$ Hz). (¹⁹F{¹H} NMR: δ - 114 (s)).

2.3.3. Ir(I) complex

¹H NMR data



The pyridyl ring was analysed as an AA'XX' system and the fluorinated ring as an AMNX system.

H_a: δ8.56, (2H, $J_{ab}=6$ Hz, $J_{aa'}=1$ Hz, $J_{ab'}\sim 0$ Hz); H_b: δ7.35 (2H, $J_{ba}=6$ Hz, $J_{bb'}=2$ Hz, $J_{ba'}\sim 0$ Hz); H_c: δ7.44 (1H, $J=16$ Hz); H_d: δ6.95 (1H, $J=16$ Hz); H_e: δ7.51 (1H, $J_{eF}=9$ Hz, $J_{cg}\sim 0$ Hz, $J_{ef}=9$ Hz); H_f: δ6.72 (1H, $J_{fg}=9$ Hz, $J_{fe}=9$ Hz, $J_{fF}\sim 0$ Hz); H_g: δ6.64 (1H, $J_{gf}=9$ Hz, $J_{gF}=12$ Hz, $J_{ge}\sim 0$ Hz); H_h: δ3.96 (t, 2H, $J=6.5$ Hz); H_i: δ1.80 (qn, 2H); H_j: δ1.45, (m, 4H); H_k: δ0.94 (t, 3H, $J=7$ Hz). (¹⁹F{¹H} NMR: δ - 114 (s)).

That the vinylic group has a *trans*-disposition is shown by $J_{HcHd}=16$ Hz.

The two materials used in this study both gave slightly less than satisfactory analytical data, although the purity of the resulting complexes is not in doubt.

2.4. Crystal structure determination [9]

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50^\circ$ on a Nicolet R3 4-circle diffractometer by the ω -scan method. The 1062 independent reflections (of 4449 measured) for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarization effects. The structure was solved by multiple solution direct methods and refined by blocked cascade least squares. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final R 0.0909

Table 1. Analytical data for the iridium complexes.

Isomer	Yield/ <i>n</i>	per cent	Microanalysis: calculated (found) per cent		
			C	H	N
2	5	61	42.2(42.1)	3.5(3.5)	2.5(2.1)
2	11	80	47.8(47.4)	4.9(4.7)	2.1(1.9)
3	5	70	42.2(41.9)	3.5(3.6)	2.5(2.3)
3	6	85	43.3(43.4)	3.8(3.7)	2.4(2.1)
3	7	76	44.3(43.9)	4.1(4.2)	2.4(2.2)
3	11	80	(47.9(48.4)	4.9(4.9)	2.1(2.0)

Table 2. Analytical data for 3-fluorostilbazoles.

n	Yield/ per cent	m.p./°C	Microanalysis: calculated (found) per cent		
			C	H	N
1	35	84	73.4 (73.4)	5.3 (5.2)	6.1 (5.8)
2	52	97	74.0 (74.0)	5.8 (5.8)	5.8 (5.6)
3	13	85	74.7 (74.3)	6.3 (6.3)	5.4 (5.2)
4	29	63	75.3 (75.5)	6.7 (6.7)	5.2 (5.0)
5	50	69	75.8 (75.7)	7.1 (7.0)	4.9 (4.9)
6	59	56	76.2 (76.4)	7.4 (7.2)	4.7 (4.5)
7	48	78	76.7 (76.6)	7.7 (7.8)	4.5 (4.4)
8	32	64	77.0 (76.9)	8.0 (7.9)	4.3 (4.1)
9	56	85	77.4 (77.1)	8.3 (8.2)	4.1 (3.9)
10	45	70	77.7 (77.6)	8.5 (8.5)	3.9 (3.7)
11	53	86	78.0 (77.7)	8.7 (8.7)	3.8 (4.1)
12	45	69	78.3 (77.8)	8.4 (8.6)	3.7 (3.4)

Table 3. Atom coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$).

Atom	x	y	z	U_{eq}^\dagger
F(1)	14258(7)	9095(3)	1364(2)	101(2)
N(1)	20811(13)	14869(6)	2696(3)	89(4)
O(1)	10532(8)	9268(4)	831(2)	89(3)
C(1)	21428(15)	13954(7)	2676(4)	105(5)
C(2)	20227(13)	13199(5)	2449(3)	95(4)
C(3)	18217(12)	13356(6)	2212(3)	69(4)
C(4)	17520(14)	14316(6)	2229(4)	84(4)
C(5)	18850(17)	15016(7)	2468(4)	99(5)
C(6)	16980(11)	12525(5)	1971(3)	77(4)
C(7)	15055(10)	12537(5)	1708(3)	80(4)
C(8)	13861(11)	11703(5)	1484(3)	67(3)
C(9)	14674(11)	10763(5)	1535(3)	78(4)
C(10)	13490(14)	10023(5)	1315(3)	81(4)
C(11)	11497(15)	10097(7)	1038(4)	72(4)
C(12)	10681(12)	11031(6)	994(3)	77(4)
C(13)	11851(10)	11799(5)	1218(3)	87(4)
C(14)	8435(10)	9318(5)	577(3)	87(4)
C(15)	7820(12)	8275(5)	438(3)	88(4)
C(16)	5646(13)	8152(6)	121(3)	84(4)
C(17)	5212(12)	7082(5)	-31(3)	84(4)
C(18)	3051(11)	6883(5)	-326(3)	78(4)
C(19)	2664(10)	5819(5)	-476(3)	79(4)
C(20)	504(10)	5622(5)	-771(3)	82(4)
C(21)	100(12)	4560(5)	-919(3)	83(4)
C(22)	-2061(13)	4392(6)	-1231(3)	88(5)
C(23)	-2506(12)	3357(6)	-1411(3)	100(5)
C(24)	-4667(11)	3240(6)	-1723(3)	117(5)

† Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

(R_w 0.0677, 244 parameters; mean and maximum final Δ/σ were 0.008 and 0.032 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron density synthesis showed minimum and maximum values of -0.25 and $+0.24 \text{ e \AA}^{-3}$. Complex scattering factors were taken from the program package SHELXTL [10] as implemented on the Data General Nova 3 computer. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00013(F)^2]$ was used in the latter stages of the refinement. Table 3 lists atomic positional parameters with estimated standard deviations.

Crystal data for 11-3F-OPhVPy; $\text{C}_{24}\text{H}_{32}\text{FNO}$; $M = 369.58 \text{ g mol}^{-1}$; crystallized from pentane/methanol as colourless, elongated plates; crystal dimensions $0.55 \times 0.25 \times 0.125 \text{ mm}$. Monoclinic, $a = 6.522(8)$, $b = 13.914(21)$, $c = 24.492(20) \text{ \AA}$, $\beta = 96.75(9)^\circ$, $U = 2207(5) \text{ \AA}^3$; $D_c = 1.112 \text{ g cm}^{-3}$, $Z = 4$. Space group $\text{P}2_1/c$ (C_{2h}^5 , No. 14), MoK_α radiation ($\lambda = 0.71069 \text{ \AA}$), $\mu(\text{MoK}_\alpha) = 0.68 \text{ cm}^{-1}$, $F(000) = 795.89$.

3. Results and discussion

3.1. Structure and properties of the fluorinated stilbazoles

Unlike the unsubstituted stilbazoles which were weakly mesomorphic, none of the fluorinated analogues showed a mesophase. The disappearance of the relatively wide range crystal E phase may possibly be attributed to the observation that lateral substitution can suppress more ordered smectic phases [1(c)], while the loss of the S_B phase may be due to the general destabilization of clearing temperatures due to the broadening of the molecule resulting from the incorporation of fluorine. The melting points of the 3-fluorinated materials (see table 2) were between 10 and 20°C lower than the clearing points of the non-fluorinated systems [8] and the former showed a marked odd-even effect.

For each of the two fluorinated materials, there are in principle two extreme rotational conformers possible, assuming that both are *trans* about the vinylic double bond, although (2B) is almost certainly precluded on steric grounds (see figure 3). ^1H and ^{19}F NMR studies of the materials revealed only one species in solution; this was attributed to the fast rotation ($\approx 10^8 \text{ s}^{-1}$) expected about the bond between the vinyl group and the ring containing the fluorine, thereby rapidly interconverting the two conformers [11]. However, single crystal X-ray diffraction studies of one of the 3-fluorostilbazoles (see below) showed only one conformer in the chosen crystal.

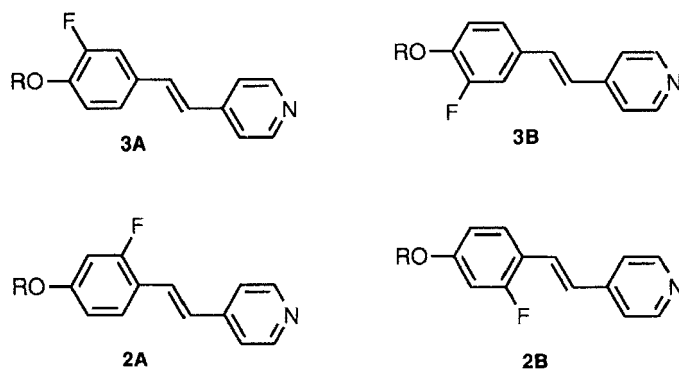


Figure 3. Possible conformers for the fluorinated stilbazoles.

3.2. Molecular structure of 4-undecyloxy-3-fluoro-4'-stilbazole

The molecular structure of 4-undecyloxy-3-fluoro-4'-stilbazole is illustrated in figure 4: bond lengths and angles with estimated standard deviations are given in tables 4 and 5 respectively. The molecule comprises a stilbazole fragment carrying a terminal undecyloxy substituent and a fluorine in a position *ortho* to the alkoxy chain. The crystal structure involves only one of the two possible extreme rotational conformers based on the *trans*-configuration (see **3B** in figure 3 and the structure in figure 4 where the disposition of the ring–F and C=C bonds is made clear). The two aromatic rings are each planar (r.m.s. deviations 0.002 and 0.006 Å) and are twisted with respect to the plane of the alkenic moiety (r.m.s. deviation 0.007 Å) by 4 and 1°, and are mutually twisted by 4° (see figure 5). The conformation of the undecyloxy chain is antiperiplanar throughout, with successive torsion angles +176, –176, –176, +177, +178, +180, +180, –180, –178, +177, –179°.

3.3. Complexes of the fluorinated stilbazoles with Ir(I)

Iridium complexes were chosen for study as they are more stable in the mesophase than their rhodium congeners and because the mesomorphism of the Rh(I) and Ir(I) systems was very similar. Unfortunately however, none of the materials synthesized showed an enantiotropic mesophase. Thus, the complexes *cis*-[IrCl(CO)₂(5-2F-OPhVPy)] and *cis*-[IrCl(CO)₂(11-2F-OPhVPy)] showed a monotropic nematic (T_{NI}

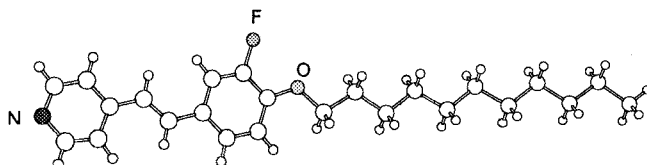


Figure 4. Molecular structure of 11-3F-OPhVPy.

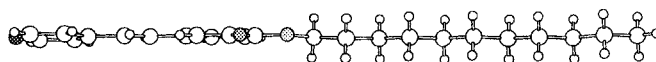


Figure 5. Side view of 11-3F-OPhVPy.

Table 4. Bond lengths (Å).

Bond	Length/Å	Bond	Length/Å
F(1)–C(10)	1.385(9)	N(1)–C(1)	1.337(12)
N(1)–C(5)	1.350(14)	O(1)–C(11)	1.381(11)
O(1)–C(14)	1.437(8)	C(1)–C(2)	1.388(12)
C(2)–C(3)	1.387(11)	C(3)–C(4)	1.413(12)
C(3)–C(6)	1.492(11)	C(4)–C(5)	1.387(13)
C(6)–C(7)	1.342(9)	C(7)–C(8)	1.468(10)
C(8)–C(9)	1.411(10)	C(8)–C(13)	1.400(9)
C(9)–C(10)	1.360(11)	C(10)–C(11)	1.397(13)
C(11)–C(12)	1.404(13)	C(12)–C(13)	1.389(11)
C(14)–C(15)	1.533(10)	C(15)–C(16)	1.544(11)
C(16)–C(17)	1.552(11)	C(17)–C(18)	1.532(10)
C(18)–C(19)	1.539(10)	C(19)–C(20)	1.530(9)
C(20)–C(21)	1.538(10)	C(21)–C(22)	1.540(11)
C(22)–C(23)	1.524(12)	C(23)–C(24)	1.532(10)

Table 5. Bond angles.

Bonds	Angle/°	Bonds	Angle/°
C(1)–N(1)–C(5)	113.8(8)	C(11)–O(1)–C(14)	119.2(6)
N(1)–C(1)–C(2)	125.2(8)	C(1)–C(2)–C(3)	120.6(8)
C(2)–C(3)–C(4)	115.4(7)	C(2)–C(3)–C(6)	119.0(7)
C(4)–C(3)–C(6)	125.7(7)	C(3)–C(4)–C(5)	119.3(8)
N(1)–C(5)–C(4)	125.6(9)	C(3)–C(6)–C(7)	127.7(7)
C(6)–C(7)–C(8)	126.5(7)	C(7)–C(8)–C(9)	121.5(6)
C(7)–C(8)–C(13)	121.6(6)	C(9)–C(8)–C(13)	116.9(6)
C(8)–C(9)–C(10)	118.5(7)	F(1)–C(10)–C(9)	119.3(7)
F(1)–C(10)–C(11)	114.6(7)	C(9)–C(10)–C(11)	126.1(8)
O(1)–C(11)–C(10)	118.4(8)	O(1)–C(11)–C(12)	126.3(8)
C(10)–C(11)–C(12)	115.3(8)	C(11)–C(12)–C(13)	119.8(7)
C(8)–C(13)–C(12)	123.4(7)	O(1)–C(14)–C(15)	105.1(5)
C(14)–C(15)–C(16)	114.7(6)	C(15)–C(16)–C(17)	111.0(6)
C(16)–C(17)–C(18)	114.7(6)	C(17)–C(18)–C(19)	113.7(6)
C(18)–C(19)–C(20)	113.6(6)	C(19)–C(20)–C(21)	114.0(6)
C(20)–C(21)–C(22)	112.6(6)	C(21)–C(22)–C(23)	114.7(7)
C(22)–C(23)–C(24)	112.2(7)		

at 89°C) and S_A (T_{SAI} at 119°C) phase respectively, while *cis*-[IrCl(CO)₂(5-3F-OPhVPy)], *cis*-[IrCl(CO)₂(6-3F-OPhVPy)], *cis*-[IrCl(CO)₂(7-3F-OPhVPy)] and *cis*-[IrCl(CO)₂(11-3F-OPhVPy)] were non-mesomorphic.

In order to quantify the extent of phase destabilization in the 3-fluoro isomers, a phase diagram was constructed for various mixtures of *cis*-[IrCl(CO)₂(6-3F-OPhVPy)] with its non-fluorinated analogue (see figure 6). The diagram showed that as the percentage of *cis*-[IrCl(CO)₂(6-3F-OPhVPy)] was increased, the nematic phase was gradually destabilized and its virtual T_{NI} was obtained by extrapolation, assuming a linear relationship between composition and clearing point for the mixtures. Thus, the virtual T_{NI} for *cis*-[IrCl(CO)₂(6-3F-OPhVPy)] at 85.5°C was some 25°C lower than the T_{NI} of its non-fluorinated analogue. Curiously, the phase diagram showed no evidence of eutectic behaviour in the melting point and indeed, fluorination of the ligand appears to have little effect on the melting point of the complexes.

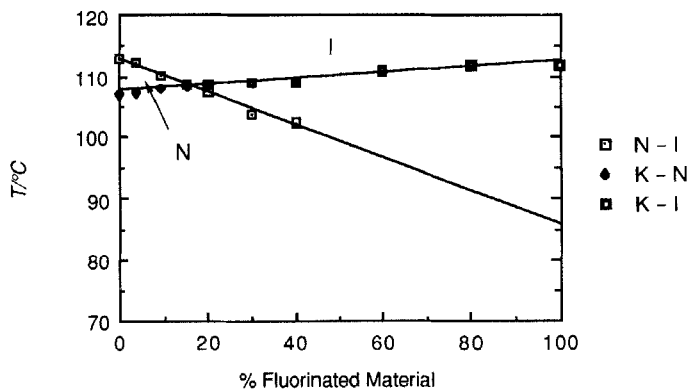


Figure 6. Phase diagram for mixtures of [IrCl(CO)₂(6-OPhVPy)] and [IrCl(CO)₂(6-3F-OPhVPy)].

These results contrast with the results obtained for silver(I) complexes of the same fluorinated ligands [12]. In these systems, the 2-fluoro isomers were found to promote the occurrence of nematic and cubic phases of the materials, while destabilizing the smectic A phase, while for the 3-fluoro isomers, the nematic and cubic phases were very strongly destabilized and the S_A phase was promoted.

The reasons for the destabilizing effects seen in these Ir(I) complexes is not clear. While it is possible to construct arguments based on preferred conformations of both the fluorine-bearing ring and the alkoxy chain, these are not necessarily felt to be very helpful. An alternative explanation may rest with the different dipolar nature of the fluorinated complexes which would, of course, strongly affect the nature of the intermolecular interactions determining mesomorphism. Such conclusions must await further studies of simple, dipolar metallo-mesogens and related systems.

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