Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Hydrogen-bonded oxadiazole mesogens

Pamela J. Martin[a]; Duncan W. Bruce[a]
[a] Department of Chemistry, University of York, Heslington, York YO10 5DD, UK

To cite this Article Martin, Pamela J. and Bruce, Duncan W.(2007) 'Hydrogen-bonded oxadiazole mesogens', Liquid Crystals, 34: 6, 767 — 774

To link to this Article: DOI: 10.1080/02678290701343273

URL: http://dx.doi.org/10.1080/02678290701343273

Liquid Crystals, Vol. 34, No. 6, June 2007, 767–774

Hydrogen-bonded oxadiazole mesogens

PAMELA J. MARTIN and DUNCAN W. BRUCE*
Department of Chemistry, University of York, Heslington, York YO10 5DD, UK

(*Received 19 January 2007; accepted 22 February 2007*)

Hydrogen-bonded analogues of recently reported biaxial nematic oxadiazoles have been prepared. These are obtained by having oxadiazole derivatized with either one or two pyridines, leading either to symmetric or unsymmetric materials complexed using several different benzoic acids. The new materials were studied by optical microscopy and DSC and were found to show N and SmA phases, i.e. mesomorphism characteristic of a calamitic rather than a bent-core mesogen. This mesomorphism is discussed in terms of the flexibility of the complexes and the bend angle at the centre of the complexes.

1. Introduction

For many years perceived wisdom insisted that liquid crystals were formed of rod- or disc-shaped mesogens, yet examination of the literature shows that there are several examples of bent systems, notably derivatized catechols and 2,5-cyclopentanones [1]. Interest in such non-conventional materials increased significantly in the mid-1990s following the report of spontaneous symmetry breaking in lamellar phases of 1,3-disubstituted benzenes by Niori *at al.* [2]; recently, this general area has been very well reviewed [3]. Spontaneous symmetry breaking in these materials relied at one level on the fact that the molecules had approximate C_{2v} symmetry (compared with D_∞ or $D_{\infty h}$ for conventional, calamitic systems), so that the packing of such objects into layers in a tilted manner allows the symmetry to be broken.

Bent-core materials also generated a good deal of interest in the theoretical and computational communities, and a wealth of potential new phases emerges from their treatments [4]. In particular, it is interesting that these studies have predicted both symmetry breaking and the formation of a biaxial phase in the nematic phases of these materials. This is particularly noteworthy following reports of an N_B phase in bent-core oxadiazole mesogens [5] (see figure 1) and of the experimental observation of spontaneous symmetry breaking in the nematic phase of these materials [6, 7].

An important parameter in these bent-core systems in the bend angle, for empirically it is observed that too small an angle suppresses mesomorphism totally, while as the angle increases past 120°, there is a point at which the mesomorphism becomes that of a conventional calamitic system [8]. Interestingly, such effects may also be induced in flexibly linked dimers where the flexible chain has an odd parity [9]. However, in regard to this question of angle, it is interesting to note a very recent reports of an N_B phase in a molecule with a 90° central angle, something that would, intuitively, have been expected not to be mesomorphic [10].

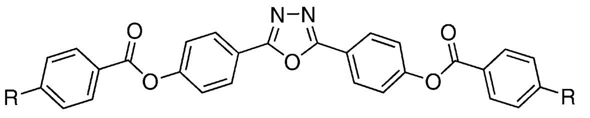
Like many others, we were intrigued by the reports of an N_B phase in oxadiazole systems, not least because the bend angle was probably fairly close to the point at which the mesomorphism of calamitic materials might have been expected. For example, 2,5-disubstituted thiophenes have been shown to behave as calamitic materials on several occasions [11]. Thus, it seems that the dipolar nature of the oxadiazole core may be significant in influencing the mesomorphism, something supported by a recent atomistic simulation [12].

However, one experimental difficulty that accompanies further study of the oxadiazole systems is their high transition temperatures and the fact that in air at the upper reaches of mesophase behaviour, including the nematic phase, the materials degrade slowly. Thus, in order to try to realize analogous materials with more easily accessible transition temperatures, we designed and prepared two series of oxadiazole mesogens in which one or both of the ester functions was replaced by a hydrogen-bonded unit [13]. In some previous work on hydrogen-bonded mesogens, we had noted a structural analogy between a diaryl ester function and a hydrogen-bonded unit consisting of a benzoic acid and a pyridine, and we noted the ability of the latter to generate materials with much lower transition temperatures [14]. Further, during the course of our work, a report appeared from the Zaragoza group that showed that

---

*Corresponding author. Email: db519@york.ac.uk

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701343273



A R = C_7H_{15}–
B R = $C_{12}H_{25}O$–

Figure 1. 'Parent' oxadiazoles.

mesophases of bent-core mesogens might be realized in hydrogen-bonded systems [15].

2. Results and discussion

2.1. *Synthesis*

In the target acceptor units, the oxadiazole ring would be retained at the core, being functionalized in the 2- and 5-positions so that there was either one or two pyridine rings available for hydrogen bonding. The pyridine-containing products (**5** and **9**) and their syntheses are shown in figures 2 and 3.

The preparation of the two target molecules was carried out following the general approach described by Görtz and Goodby [7], and used methodology employed by Zhao and Burke [16] and by Tanaka *et al.* [17]. Thus, in preparing **5**, the pentafluorophenyl ester of pyridine-4-carboxylic acid (**1**) was reacted with the semihydrazone of the same acid (**2**) to give the symmetric hydrazide (**3**). Ring closure was effected by dehydration using thionyl chloride, giving the product as its dihydrochloride (**4**), which was finally neutralized using aqueous base. The yield for each step was >80% except for the formation of **2**, which proceeded with ca. 60% recovery of product.

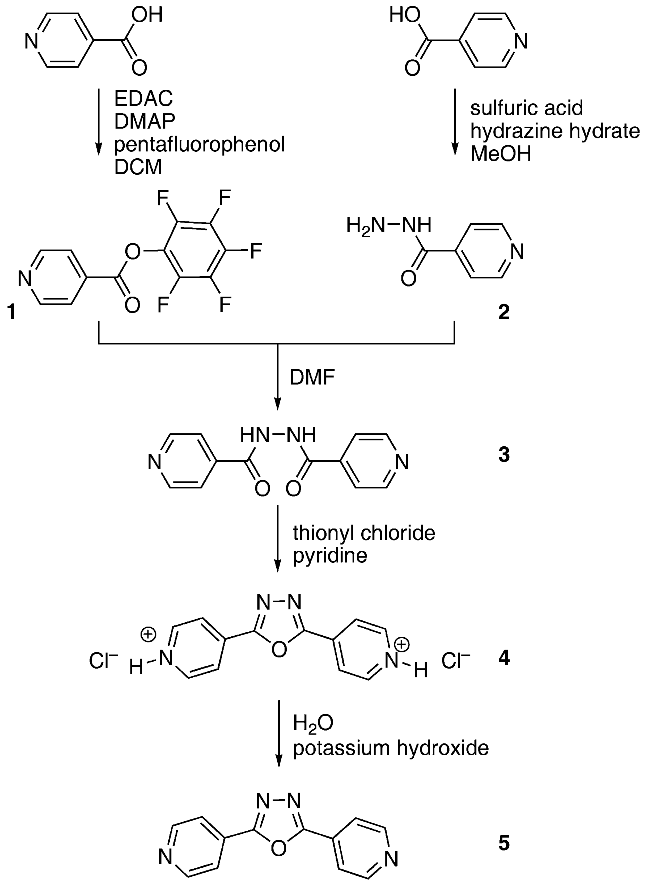


Figure 2. Synthesis of the symmetric 2,5-di(4′-pyridyl)-1,3,4-oxadiazole (**5**).

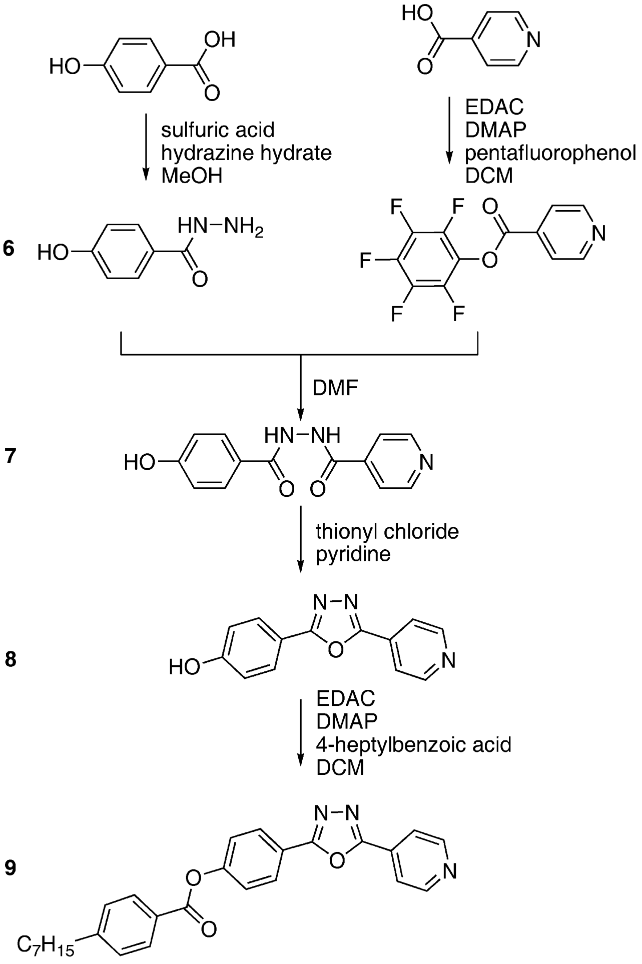
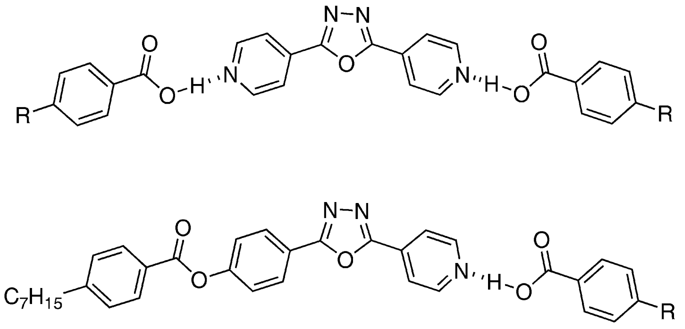


Figure 3. Synthesis of the unsymmetric 2-(4′-pyridyl)-5-(4‴-heptylbenzoyloxy-4″-phenyl)-1,3,4-oxadiazole (**9**).

The preparation of **9** followed an identical methodology with the exceptions that the semihydrazide (**6**) was now derived from 4-hydroxybenzoic acid and that following cyclization, the pyridine (**8**) was recovered unprotonated; esterification with 4-heptylbenzoic acid



10

11

	R		R
a	OC_6H_{13}	**g**	C_6F_{13}
b	OC_8H_{17}	**h**	Ph–C_8H_{17}
c	$OC_{10}H_{21}$	**i**	CF_3
d	$OC_{12}H_{25}$	**j**	CH_3
e	$OC_{16}H_{33}$	**k**	F
f	C_7H_{15}	**l**	NO_2
		m	CN

Figure 4. Structure of the new complexes.

completed the synthesis. Yields in this scheme were generally lower, ranging from 55-80% for most steps.

Hydrogen-bonded complexes were obtained for **5** and **9** to give **10** and **11**, respectively, following a common methodology (figure 4). For example for **10**, one molar equivalent of **5** and two molar equivalents of the corresponding benzoic acid would be dissolved separately in THF before the two solutions were combined and stirred. Complexes were then obtained either by simply removing the THF *in vacuo* or by crystallization. Complexes **11** were obtained analogously using a 1:1 molar ratio of **9** and the benzoic acid.

2.2. *Liquid crystal properties*

Compound **9** and complexes **10** and **11** were examined by polarizing optical microscopy and DSC to determine their mesomorphism (**5** was non-mesomorphic, simply melting at 187°C); thermal data for **10** and **11** are collected in tables 1 and 2, respectively. In choosing the benzoic acids, five were related as simple homologues (**a**–**e**), whereas the remainder contained different chains (**f**–**h**) or small, terminal groups (**i**–**m**). Parent pyridine **9** was found to be mesomorphic on its own and showed an enantiotropic nematic phase (Cr • 136.0 [36.3] • N • 149.1 [0.2] • I; transition enthalpies (kJ mol^{-1}) in square brackets) with a strong tendency to homeotropy between glass cover slips. Below the nematic phase was a monotropic SmA phase (SmA • 128.2 [0.3] • N), which was also homeotropic.

Complexes **10a** to **10e** are related as homologues and all show a SmA phase. For **10c** to **10e** this is enantiotropic and is narrow in range, whereas for **10a** and **10b**, it is monotropic. Owing to their poor mesomorphic properties, these symmetric complexes were not investigated further and so attention turned to the unsymmetric complexes derived from pyridine **9**.

Complexes **11** showed a more extensive mesomorphism with wider mesomorphic ranges. Complexes **11a** to **11e** are related as homologues and their mesomorphism is represented diagrammatically in figure 5. The melting points (mostly between 125 and 130°C) decrease with increasing alkoxy chain length and the first two homologues (n=6 and 8) show both a SmA and a N

Table 1. Thermal data for the symmetric complexes, **10**.

Compound	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
10a	Cr–I	142.3	81.9	197
	(SmA–I)	(137.0)	–[†]	–
10b	Cr–I	142.1	61.3	148
	(SmA–I)	(140.5)	(10.5)	25
10c	Cr–SmA	135.4	40.4	99
	SmA–I	142.0	13.7	33
10d	Cr–SmA	134.9	53.4	131
	SmA–I	142.7	14.5	35
10e	Cr–SmA	133.1	47.5	117
	SmA–I	139.5	15.3	37
10f	Cr–I	141.6	45.7	110
10g	Cr–Cr’	170.4	4.1	9
	Cr’–I	183.9	54.7	120
10h	Cr–SmA	186.6	31.4	68
	SmA–I	211.6	16.9	35

[†] Not seen by DSC.

Table 2. Thermal data for the unsymmetric complexes, **11**.

Compound	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
11a	Cr–Cr’	126.8	30.5	76
	Cr’–SmA	137.8	35.6	87
	SmA–N	148.7	1.1	3
	N–I	158.4	2.2	5
11b	Cr–Cr’	121.4	19.0	48
	Cr’–SmA	129.8	18.9	47
	SmA–N	152.8	1.1	3
	N–I	157.7	1.9	4
11c	Cr–Cr’	118.5	20.3	52
	Cr’–SmA	129.3	27.1	67
	SmA–I	153.4	7.4	17
11d	Cr–Cr’	118.6	17.1	44
	Cr’–SmA	127.2	14.8	37
	SmA–I	154.7	8.9	21
11e	Cr–Cr’	114.4	58.9	152
	Cr–SmA	123.9	11.2	28
	SmA–I	153.2	11.5	27
11f	Cr–SmA	138.2	25.5	62
	SmA–I	149.4	4.7	11
11g	Cr–SmA	179.8	32.6	72
	SmA–dec	215.4	16.6	34
11h	Cr–SmA	167.1	47.9	109
	SmA–N	190.6	0.7	2
	N–I	202.0	3.2	7
11i	Cr–SmA	155.8	34.3	80
	SmA–I	189.0	10.0	22
11j	Cr–I	163.2	55.1	126
	(N–I)	(163.1)	(1.2)	(3)
	(SmA–N)	(152.8)	(1.2)	(3)
11k	Cr–Cr’	137.2	12.7	31
	Cr’–SmA	143.9	19.2	46
	SmA–dec	169.6	7.8	18
11l	Cr–SmA	161.8	32.1	74
	SmA–N	180.2	1.7	4
	N–dec	186.8	0.9	2
11m	Cr–SmA	152.5	25.5	60
	SmA–N	168.4	0.7	2
	N–dec	184.8	1.8	4

phase; higher homologues show only the SmA phase. With the exception of **11a**, the stability of the SmA phase is seen to be relatively insensitive to the alkoxy chain length, disappearing on average around 154°C. Given this more extensive mesomorphism, a further series of complexes was prepared (**11f** to **11m**)

Changing alkyloxy to alkyl (**11f**) had little effect on the thermal behaviour, except that the crystal phase was stabilized so reducing the range of the SmA phase; by comparison, using a perfluorohexyl chain (**11g**) stabilized both the crystal and SmA phases hugely. Extending the anisotropy of the system with octylbiphenylcarboxylic acid (**11h**) gave high-temperature N and SmA phases.

The remaining complexes employed benzoic acids bearing more or less polar groups in the 4-position. The relatively non-polar *p*-toluic acid (**11j**) led to a material with a nematic phase that was just monotropic (Cr–I at 163.2°C, N–I at 163.1°C), below which was found a SmA phase. 4-Nitrobenzoic acid (**11l**) and 4-cyanobenzoic acid (**11m**) both led to complexes with enantiotropic N and SmA phases, while 4-trifluoromethylbenzoic acid (**11i**) and 4-fluorobenzoic acid (**11k**) gave complexes with a SmA phase. The stabilizing effect of these polar benzoic acids is noteworthy as all but one complex formed from them show melting points at or above the clearing points of the simple 4-alkoxybenzoic acids (**11a** to **11e**). Another interesting observation is that almost all of the

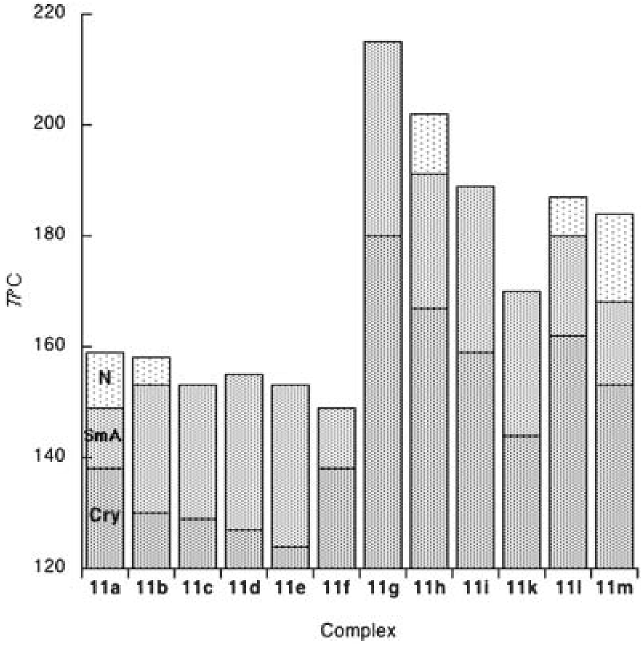


Figure 5. Representation of the mesomorphism of hydrogen-bonded complexes (**11**) (**11j** is omitted as its mesophases are monotropic).

complexes **11** show an overall mesomorphic range within the range 31 ± 4°C.

2.3. *Discussion*

Initial results with the symmetrically hydrogen-bonded complexes (**10**) showed only weakly or non-mesomorphic materials, with the SmA phase being the only phase seen. The nature of the mesomorphism, *i.e.* one characteristic of a calamitic mesogen, is attributed to the fact that there are two, flexible hydrogen bonded units, which open up the central bend angle. It was then reasoned that if the unsymmetric analogues, **11**, were accessed, the presence of one, fixed ester group may tighten the central angle sufficiently to restore mesomorphism characteristic of a bent-core system. Clearly, this was not the case and once more the mesomorphic properties were dominated by the formation of a SmA phase, with some complexes showing a nematic phase, too.

What is, however, interesting is that almost without exception, the transition temperatures of the unsymmetric complexes, **11**, are higher than those of symmetric **10**. Normally, it is expected that symmetric materials pack more efficiently in both the crystal and liquid crystal state so that their transition temperatures are higher than those of related materials of lower symmetry. This difference is attributed to the greater flexibility of complexes **10** due to the presence of two hydrogen-bonded groups, which clearly lowers both the clearing and the melting points.

What we conclude, therefore, is that in the parent oxadiazole compounds (figure 1), the central angle is actually rather close to the point at which the mesomorphism would change from that of a bent-core to a calamitic mesogen. Thus, a relatively small opening up of this angle *via* the replacement of an ester function by a hydrogen-bonded unit, 'flips' the mesomorphism to that of a calamitic system.

Further, we would speculate that the central angle in these parent oxadiazoles is too large to accommodate bent-core behaviour under normal circumstances and that the strongly dipolar nature of the oxadiazole unit is crucial in determining the exact nature of the phase behaviour. These assertions are supported by a recent atomistic simulation of parent oxadiazole **A**, which showed that removing the charges on the molecule suppressed the formation of the lower-symmetry nematic phase [12]. This being the case, it is interesting to speculate whether analogous materials with similarly large transverse dipoles and smaller central angles would give rise to lower-symmetry nematic phases with larger order parameters.

3. Experimental

3.1. *Materials and characterization*

New compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy recorded on a JEOL ECX400 or JEOL EX270 spectrometers, whereas ^{19}F spectra were recorded on the latter instrument. Elemental analysis was carried out at the University of Newcastle.

Differential scanning calorimetry used a Mettler Toledo DSC822^{e} with Mettler Toledo TS0801RO Sample Robot, calibrated against pure indium metal. Heating and cooling rates were 5°C min^{-1}.

An Olympus BX50 polarizing microscope equipped with a Linkam scientific LTS350 heating stage, Linkam LNP2 cooling pump and Linkam TMS92 controller was used to observe the optical textures and thermal transitions of all the materials.

3.2. *Synthesis*

3.2.1. Perfluorophenyl isonicotinate. *N*-Ethyl-*N*′-dimethylaminopropylcarbodiimide hydrochloride (EDAC, 0.96 g, 5.0 mmol), 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 0.2 g) and pentafluorophenol (1.0 g, 5.44 mmol) were dissolved in dry dichloromethane (30 cm^{3}) in an inert atmosphere.

Isonicotinic acid (0.62 g, 5.0 mmol) was dissolved in a mixture of dry dichloromethane/toluene (90 cm^{3}; 6:3) and then added to the mixture and the solution was left under reflux overnight. Once cooled, the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) eluted with DCM and crystallized from hexane: diethyl ether (7:3 v/v) and dried under vacuum to yield the product as a colourless solid (1.19 g, 82%). ^{1}H NMR (270 MHz, $CDCl_3$): δ=8.06 (AA'XX', 2H, *J*=5.0 Hz), 8.91 (AA'XX', 2H, *J*=5.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ=123.8 (CH_d), 125.9 (C), 133.4 (2CF), 135.6 (CF), 141.2 (2CF), 137.7 (C), 149.1 (CH_c), 164.3 (C=O). ^{19}F NMR (254 MHz, $CDCl_3$): δ=−171.2 (CF), −164.5 (CF), −162.7 (CF). Elemental analysis (%): found C 50.0, H 1.4, N 4.76 for $C_{12}H_4NO_2F_5$; required C 49.8, H 1.39, N 4.84.

3.2.2. Isonicotinic acid hydrazide. Isonicotinic acid (2.76 g, 22.4 mmol) was dissolved in methanol (100 cm^3) under an atmosphere of nitrogen. A few drops of sulfuric acid (conc., ca. 0.15 cm^3) was added to the solution before the temperature was raised to reflux and held there for 8 h. Hydrazine hydrate (98%, 2.5 cm^3, 45 mmol) was added to the hot solution and reflux was continued overnight. The reaction mixture was then cooled to room temperature and the solvent removed under vacuum. Ice-cold water (200 cm^3) was poured onto the resulting solid, which was then filtered before crystallization from ethanol to yield the product as a pure, colourless solid (1.93 g, 63%). ^{1}H NMR (270 MHz, DMSO): δ=4.62 (s, 2H, NH_2), 7.72 (AA'XX', 2H, *J*=5.6 Hz, Ar-H), 8.69 (AA'XX', 2H, *J*= 5.6 Hz, Ar-H), 10.09 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO): δ=121.0 (CH), 140.3 (C), 150.2 (CH), 163.9 (C=O). Elemental analysis (%): found C 52.6, H 5.2, N 30.8 for $C_6H_7N_3O$; required C 52.6, H 5.1, N 30.6.

3.2.3. *N'*-Isonicotinoylisonicotinohydrazide. Isonicotinohydrazide (1.06 g, 7.73 mmol) and perfluorophenyl isonicotinate (2.24 g, 7.73 mmol) were placed in a flask flushed previously with nitrogen. Anhydrous dimethylformamide (18 cm^3) was added and the solution left to stir overnight at room temperature.

The solvent was removed under high vacuum and the resultant solid crystallized from ethyl acetate until pure, colourless *N'*-isonicotinoylisonicotinohydrazide was obtained (1.85 g, 99%). ^{1}H NMR (270 MHz, DMSO): δ=7.81 (AA'XX', 4H, *J*=5.9 Hz, Ar-H), 8.79 (AA'XX', 2H, *J*=5.9 Hz, Ar-H), 10.97 (s, 2H, NH). ^{13}C NMR (100 MHz, DMSO): δ=121.31 (CH), 139.7 (C), 150.5 (CH), 164.28 (C=O). Elemental analysis (%): found C 59.5, H 4.3, N 23.4 for $C_{12}H_{10}N_4O_2$; required C 59.5, H 4.2, N 23.1.

3.2.4. 4,4′-(1,3,4-Oxadiazole-2,5-diyl)dipyridinium dichloride. Thionyl chloride (0.31 cm^3, 0.5 g, 4.20 mmol) and pyridine (0.03 g, 0.38 mmol) were added to *N'*-isonicotinoylisonicotinohydrazide (1.01 g, 4.17 mmol) under a nitrogen atmosphere. The solution was heated to 80°C and stirred overnight. After cooling, the reaction mixture was poured onto crushed ice. The solid was filtered off, washed with water and dried to yield a light brown, solid product (1.14 g, 92%). Elemental analysis (%): found C 48.7, H 3.4, N 19.0 for $C_{12}H_{10}Cl_2N_4O$; required C 48.5, H 3.4, N 18.9.

3.2.5. 2,5-Di(pyridin-4-yl)-1,3,4-oxadiazole (4-odp). 4,4′-(1,3,4-Oxadiazole-2,5-diyl)dipyridinium chloride (0.50 g, 1.68 mmol) was dissolved in water (5 cm^3) and an aqueous solution of potassium hydroxide (10% w/v) was added dropwise until the solution became slightly basic; during this time, the neutral product precipitated. The suspension was then extracted with chloroform (4 × 20 cm^3), after which the combined extracts were dried over magnesium sulfate, filtered and evaporated. The resultant solid was then crystallized from hexane/ethyl acetate to yield 2,5-di(pyridin-4′-yl)-1,3,4-oxadiazole as a creamy solid product (0.34 g, 90%). ^{1}H NMR (270 MHz, $CDCl_3$): δ=7.99 (AA'XX', 2H, *J*=5.8 Hz, Ar-H), 8.85 (AA'XX', 2H, *J*=5.8 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=121.2 (CH), 130.4 (C), 151.3 (CH), 163.8 (C). Elemental analysis (%): found C 64.3, H 3.8, N 25.1 for $C_{12}H_8N_4O$; required C 64.3, H 3.6, N 25.0.

3.2.6. 4-Hydroxybenzohydrazide. 4-Hydroxybenzoic acid (2.76 g, 20 mmol) was dissolved in methanol (100 cm^3) under an atmosphere of nitrogen. A few drops of sulfuric acid (conc., ca. 0.15 cm^3) were added to the solution before the temperature was raised to reflux for 8 h. Hydrazine hydrate (98%, 2.5 cm^3, 45 mmol) was added to the hot solution and the reflux was continued overnight.

The reaction was cooled to room temperature and the solvent removed by vacuum. The resulting solid was poured into ice-cold water (200 cm^3) and filtered before crystallization from ethanol to yield 4-hydroxybenzohydrazide as a pure, colourless solid (1.70 g, 63%). ^{1}H NMR (300 MHz, DMSO): δ=4.40 (s, 2H, NH_2), 6.77 (AA'XX', 2H, *J*=8.8 Hz, Ar-H), 7.68 (AA'XX', 2H, *J*=8.8 Hz, Ar-H), 9.50 (s, 1H, NH), 9.95 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO): δ=115.2 (CH), 124.3 (C), 129.2 (CH), 160.3 (C), 166.3 (C=O). Elemental analysis (%): found C 55.2, H 5.3, N 18.7 for $C_7H_8N_2O_2$; required C 55.3, H 5.3, N 18.4.

3.2.7. *N'*-Isonicotinoylisonicotinohydrazide. 4-Hydroxybenzoic acid hydrazide (1.00 g, 6.57 mmol) and perfluorophenyl isonicotinate (1.90 g, 6.57 mmol) were added together in a flask, which was then flushed with nitrogen. Anhydrous dimethylformamide (18 cm^3) was added and the solution left to stir overnight at room temperature.

The solvent was removed under high vacuum and the resultant solid was crystallized from ethyl acetate until pure, colourless *N′*-isonicotinoylisonicotinohydrazide was obtained (1.69 g, 100%). ^{1}H NMR (270 MHz, DMSO): δ=6.81 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 7.78 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 7.82 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 8.78 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 10.16 (bs, 3H, NH and OH). ^{13}C NMR (100 MHz, DMSO): δ=115.0 (CH), 121.7 (CH), 123.8 (C), 129.8 (CH), 139.9 (C), 150.3 (CH), 160.7 (C-OH), 164.5 (C=O), 165.3 (C=O). Elemental analysis (%): found C 60.9, H 4.7, N 16.4 for $C_{13}H_{11}N_3O_3$; required C 60.7, H 4.3, N 16.3.

3.2.8. 4′-(5-Pyridin-4″-yl-[1,3,4]oxadiazol-2-yl)phenol.

Thionyl chloride (0.6 cm^3, 0.98 g, 8.27 mmol) and pyridine (0.03 g, 0.38 mmol) were added to *N′*-(4-hydroxybenzoyl)isonicitohydrazide (2.0 g, 7.8 mmol) under a nitrogen atmosphere. The solution was heated to 80°C and stirred overnight. After cooling, the reaction mixture was poured onto crushed ice. The solid was filtered off, washed with water and dried to yield a light brown, solid product (1.35 g, 72%). ^{1}H NMR (270 MHz, DMSO): δ=5.35 (bs, 1H, OH), 7.02 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 8.02 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 8.32 (AA'XX', 2H, *J*=6.3 Hz, Ar-H), 8.99 (AA'XX', 2H, *J*=6.3 Hz, Ar-H). ^{13}C NMR (100 MHz, DMSO): δ=113.7 (C), 116.30 (CH), 121.8 (CH), 129.4 (CH), 130.6 (C), 141. (C), 147.6 (CH), 161.6 (COH). Elemental analysis (%): found C 65.4, H 3.8, N 17.7 for $C_{13}H_9N_3O_2$; required C 65.3, H 3.8, N 17.6.

3.2.9. 4′-(5-(Pyridin-4″-yl)-1,3,4-oxadiazol-2-yl)phenyl 4‴-(heptyloxy)benzoate.

Dicyclohexylcarbodiimide (0.87 g, 4.20 mmol), 4-(*N,N*-dimethylamino)pyridine (0.2 g) and 4′-(5-pyridin-4″-yl-[1,3,4]oxadiazol-2-yl)-phenol (1.00 g, 4.18 mmol) were dissolved in dry dichloromethane (100 cm^3) under an atmosphere of nitrogen.

4-Heptylbenzoic acid (0.92 g, 4.18 mmol) was dissolved in dry dichloromethane (50 cm^3) and added to the mixture. The solution was left to stir overnight at 40°C. Once the reaction mixture was cool, the solvent was removed by vacuum. The residue was purified by column chromatography (silica) eluted with dichloromethane and crystallized from ethyl acetate and hexane dried under vacuum to yield a colourless solid (1.02 g, 55%). ^{1}H NMR (270 MHz, $CDCl_3$): δ=0.97 (t, 3H, *J*=6.3 Hz, CH_3), 1.30 (m, 8H, CH_2), 1.64 (m, 2H, CH_2), 2.59 (t, 2H, *J*=7.4 Hz, CH_2-Ph), 7.22 (AA'XX', 2H, *J*=8.5 Hz, Ar-H), 7.31 (AA'XX', 2H, *J*=8.9 Hz, Ar-H), 7.58 (AA'XX', 4H, Ar-H), 8.11 (AA'XX', 2H, *J*=8.9 Hz, Ar-H), 8.71 (AA'XX', 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.1 (CH_3), 23.1 (CH_2), 28.9–32.4 (4CH_2), 35.8 (CH_2), 120.7 (C), 122.2 (CH), 125.8 (C), 128.4 (CH), 128.8 (CH), 130.4 (CH), 131.5 (C), 149.9 (CH), 154.3 (C), 156.1 (C), 161.8 (C), 164.4 (C=O). Elemental analysis (%): found C 73.5, H 6.3, N 9.6 for $C_{27}H_{27}N_3O_3$; required C 73.5, H 6.2, N 9.5.

3.2.10. Preparation of the hydrogen-bonded complexes.

The benzoic acid and the pyridine (sufficient to make 200 mg of product) were weighed out carefully according to the desired molar ratio (**10**: 1:1; **11**: 2:1) and dissolved separately in THF (10 cm^3). The two solutions were combined and stirred for ca. 3 h in a closed system before the material was crystallized by slowly evaporating solvent in the air.

Acknowledgements

We thank EPSRC and the University of York for funding to PJM, and Dr Verena Görtz (York) for discussions concerning some of the syntheses.

References

[1] H. Matsuzaki, Y. Matsunaga. *Liq. Cryst.*, **14**, 105 (1993); Y. Matsunaga, S. Miyamoto. *Mol. Cryst. liq. Cryst.*, **237**, 311 (1993).

[2] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe. *J. Mater. Chem.*, **6**, 1231 (1996).

[3] R.A. Reddy, C. Tschierske. *J. Mater. Chem.*, **16**, 907 (2006).

[4] See, for example, T.C. Lubensky, L. Radzihovsky. *Phys. Rev. E*, **66**, 031704 (2002); I. Dozov. *Europhys. Lett.*, **56**, 247 (2001).

[5] L.A. Madsen, T.J. Dingemans, M. Nakata, E.T. Samulski. *Phys. Rev. Lett.*, **92**, 145505 (2004); B.R. Acharya, A. Primak, S. Kumar. *Phys. Rev. Lett.*, **92**, 145506 (2004).

[6] G. Pelzl, A. Eremin, S. Diele, H. Kresse, W. Weissflog. *J. Mater. Chem.*, **12**, 2591 (2002).

[7] V. Görtz, J.W. Goodby. *Chem. Commun.*, 3262 (2005).

[8] See, for example, W. Weissflog, H.N.S. Murthy, S. Diele, G. Pelzl. *Phil. Trans. R. Soc. A*, **364**, 2657 (2006).

[9] See, for example, M. Šepelj, A. Lesac, U. Baumeister, S. Diele, H.L. Nguyen, D.W. Bruce. *J. Mater. Chem.*, **17**, in press (2007); M. Šepelj, A. Lesac, U. Baumeister, S. Diele, D. W. Bruce, Z. Hameršak. *Chem. Mater.*, **18**, 2050 (2005); J. Watanabe, H. Komura, T. Niiori. *Liq. Cryst.*, **13**, 455 (1993); S.W. Choi, M. Zennyoi, Y. Takanishi, H. Takazoe, T. Niori, J. Watanabe. *Mol.Cryst. liq. Cryst.*, **328**, 185 (1999); J. Watanabe, T. Izumi, T. Niori, M. Zennyoji, Y. Takanishi, H. Takezoe. *Mol. Cryst. liq. Cryst.*, **346**, 77 (2000).

[10] M. Lehmann, S.-W. Kang, C. Köhn, S. Haseloh, U. Kolb, D. Schollmeyer, Q. Wang, S. Kumar. *J. Mater. Chem.*, **16**, 4326 (2006).

[11] See, for example, S.H. Eichhorn, A.J. Paraskos, K. Kishikawa, T.M. Swager. *J. Am. chem. Soc.*, **124**, 12742

(2002); A.J. Seed, K.J. Toyne, J.W. Goodby, M. Hird. *J. Mater. Chem.*, **10**, 2069 (2000).

[12] J. Peláez, M.R. Wilson. *Phys. Rev. Lett.*, **97**, 267801 (2006).

[13] For reviews of hydrogen-bonded mesogens, see, for example, T. Kato. *Struct. Bond.*, **96**, 95 (2000); C.M. Paleos, D. Tsiourvas. *Angew. Chem. Int. Ed.*, **34**, 1696 (1995).

[14] D.J. Price, H. Adams, D.W. Bruce. *Mol. Cryst. liq. Cryst.*, **289**, 127 (1996).

[15] N. Gimeno, M.B. Ros, J.L. Serrano, M.R. de la Fuenta. *Angew. Chem. Int. Ed.*, **43**, 5235 (2004).

[16] H. Zhao, T.R. Burke Jr. *Tetrahedron*, **53**, 4219 (1997).

[17] H. Tanaka, S. Tokito, Y. Taga, A. Okada. *J. Mater. Chem*, **8**, 1999 (1998).