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Liquid Crystals

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Synthesis and liquid crystalline properties of low molecular mass compounds containing the 1,4-bis(5-phenyl-1,3,4-oxadiazolyl)benzene unit

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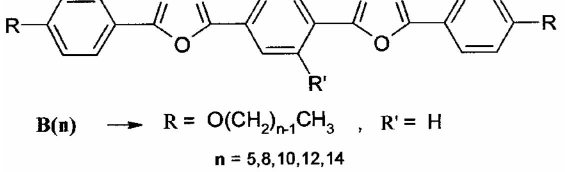
The synthesis and characterization of low molecular mass compounds containing 1,4-bis-(5-phenyl-1,3,4-oxadiazolyl)benzene is reported. All compounds are fluorescent in solution. Due to the flat shape of the conjugated unit, smectic-like packing is observed at high temperatures for some of the synthesized compounds. Moreover the insertion of a lateral flexible alkoxy unit strongly destabilizes the smectic order whilst promoting the appearance of a nematic phase in the case of the shortest methoxy unit. The mesogenic character of this unit may be of interest in the synthesis of liquid crystalline polymeric systems, taking advantage of both the fluorescent properties and the peculiar molecular structure of the liquid crystalline state.

1. Introduction

In recent years much research has focused on the investigation of new polymeric materials for application in the fields of all-optical signal processing, electro-optic devices [1–15] and organic light emitting diodes [16–33]. Conjugated polymers have attracted considerable attention because they can combine the processability and outstanding mechanical properties of polymers with the electronic and photo-physical properties of organic semiconductors.

Conjugated polymers containing the phenyl-oxadiazole unit are of great interest as they are thermally stable and possess extremely interesting electro-optical and electronic properties [23–28, 34]. It is well known that phenyl-oxadiazoles are effective electron-injecting/transporting compounds, they can show also hole-blocking properties, and moreover they can serve as emissive materials in the blue [28] as well as in the red–orange [31] spectral regions. Their application in electro-optical and highly efficient light emitting devices (LED) is a strong motivation for the fundamental investigation of structure–property relationships in this class of molecules.

Poly(phenyloxadiazole) systems can show very high glass transition temperatures and extremely good mechanical properties [35–39], which are essential prerequisites to the realization of devices. The processability of the material and its transparency are very important in order to achieve thin films of high quality. All these features can be tuned via modification of the polymer structure; for example the insertion of flexible aliphatic segments in the backbone or as pendant side chains may increase the solubility of the polymer in common organic solvents so enhancing its processability [34]. We report here the synthesis and characterisation of a new class of low molecular mass compounds containing the 1,4-bis(5-phenyl-1,3,4-oxadiazolyl)benzene unit:



B(n) → R = $O(CH_2)_{n-1}CH_3$, R' = H
n = 5,8,10,12,14

B(n,m) → R = $O(CH_2)_{n-1}CH_3$, R' = $O(CH_2)_{m-1}CH_3$
n,m = 10,1 10,5 10,9 12,1

B(N) → R = $N(CH_2CH_3)_2$, R' = H

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The main goal of the present work is the synthesis and complete characterization of this series of compounds in terms of their phase behaviour, their optical properties and fluorescence. In fact, a full understanding of the properties of the 1,4-bis(5-phenyl-1,3,4-oxadiazolyl)-benzene unit is essential in order to be able to tune the properties of oxadiazole-based polymer materials in a rational manner. Particular attention has been focused on the possibility of **B**(***n***) and **B**(***n***,***m***) to form liquid crystal phases spontaneously, similar to the behaviour reported for analogous compounds containing only one oxadiazole unit or with a short conjugation length [40–43].

2. Experimental

2.1. *Characterization*

Thermal measurements were performed using a DSC-7 Perkin Elmer calorimeter under a nitrogen flow at 10°C min^{-1}. Polarizing optical microscopy (POM) was performed using a Jenapol microscope fitted with a Linkam THMS 600 hot stage. X-ray diffraction (XRD) patterns were recorded using a flat camera with a sample-to-film distance of 140 mm (Ni-filtered Cu-Kα radiation). High temperature XRD patterns were collected using a modified Linkam THMS 600 hot stage. A Fujifilm MS 2025 imaging plate and a Fuji Bioimaging Analyser System, mod. BAS-1800, were used for recording and digitizing the diffraction patterns.

^{1}H NMR spectra were recorded using a Bruker DRX/400 Spectrometer. Chemical shifts are reported relative to the residual solvent peak (chloroform-d: $\delta_H = 7.26$ ppm, pyridine-d$_5$: $\delta_H = 7.22$, 7.58, 8.74 ppm, dimethylsulfoxide-d$_6$: $\delta_H = 2.50$). The spectra obtained were in complete agreement with the proposed structures and confirmed the purity of the compounds. UV-vis measurements were performed using a Jasco V-560 Spectrophotometer; fluorescence spectra were recorded using a Jasco FP-750 Spectrofluorometer in *N*,*N*-dimethylformamide (DMF) solutions.

2.2. *Synthesis*

All reagents and solvents were purchased from Aldrich and Carlo Erba. *N*,*N*-dimethylacetamide (DMAc) was heated at reflux over calcium hydride, distilled in vacuum and stored over 4 Å molecular sieves. Other reagents were used without further purification. Hydroxyterephthalic acid, *n*-alkoxyterephthalic acids and *n*-alkoxybenzoic acids were synthesized according to previously reported procedures [44, 45].

2.2.1. *n-Alkoxyterephthalic dihydrazides (**3**)*

Alkoxyterephthalic dihydrazides **3** were synthesized from the corresponding alkoxyterephthalic dimethylesters **2**, by reaction with an excess of hydrazine monohydrate, in ethanol solution. Thus, 14 g of *n*-alkoxyterephthalic dichloride **1** was stirred in boiling methanol (150 ml) for 2 h. The methanol was then removed under vacuum and the resulting methylester **2** used *in situ* for the subsequent reaction without further purification. The ester was dissolved in absolute ethanol (100 ml) and 100 ml of hydrazine monohydrate, diluted in 40 ml ethanol, were slowly added to the solution. The reaction was allowed to take place under reflux for 2 h. At the end the reaction system was cooled and the white, crystalline hydrazide **3** precipitated from the reaction solution. The solid was recovered by filtration, repeatedly washed with water and cold ethanol, and dried. Final yields ranged between 80 and 90%. For methoxyterephthalic dihydrazide $T_m = 245.7$°C, $\Delta H_m = 299.6$ J g^{-1}; for pentyloxyterephthalic dihydrazide $T_m = 143.0$°C, $\Delta H_m = 167.1$ J g^{-1}; for nonyloxy-terephthalic dihydrazide $T_m = 138.3$°C, $\Delta H_m = 199.1$ J g^{-1}.

2.2.2. *Terephthalic dihydrazide (**3**, with $R' = H$)*

Dimethylterephthalate **2** (with $R' = \mathrm{H}$) (8 g, 0.0412 mol) and hydrazine monohydrate (20 ml) were heated at reflux in 50 ml of toluene, for 3 h. The resulting terephthalic dihydrazide was collected by filtration, repeatedly washed with methanol, water and ethanol, and then dried. The final yield was 90%. $T_m = 336.0$°C, $\Delta H_m = 458.7$ J g^{-1}.

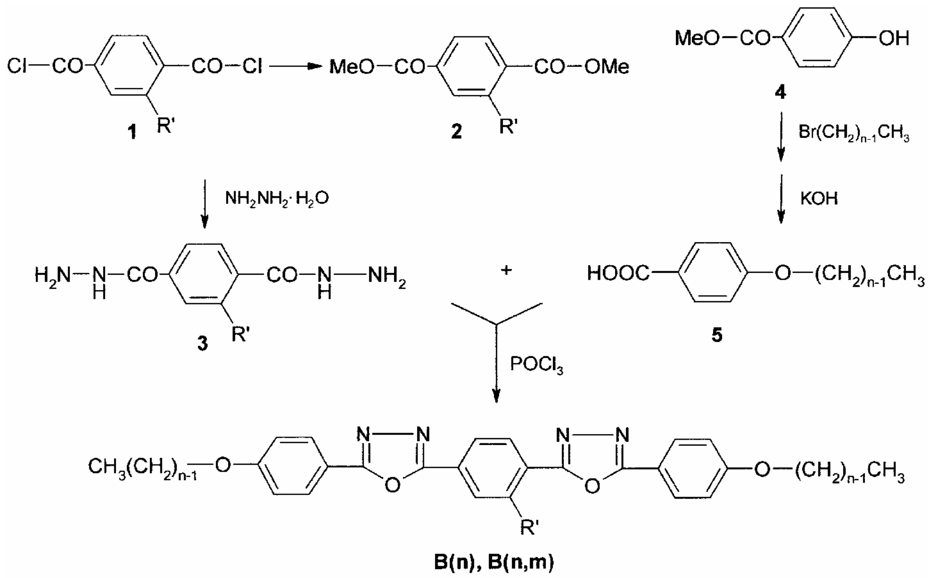
2.2.3. ***B(n)** and **B(n,m)** compounds*

The **B**(***n***) and **B**(***n***,***m***) model compounds were obtained using two different procedures shown in schemes 1 and 2.

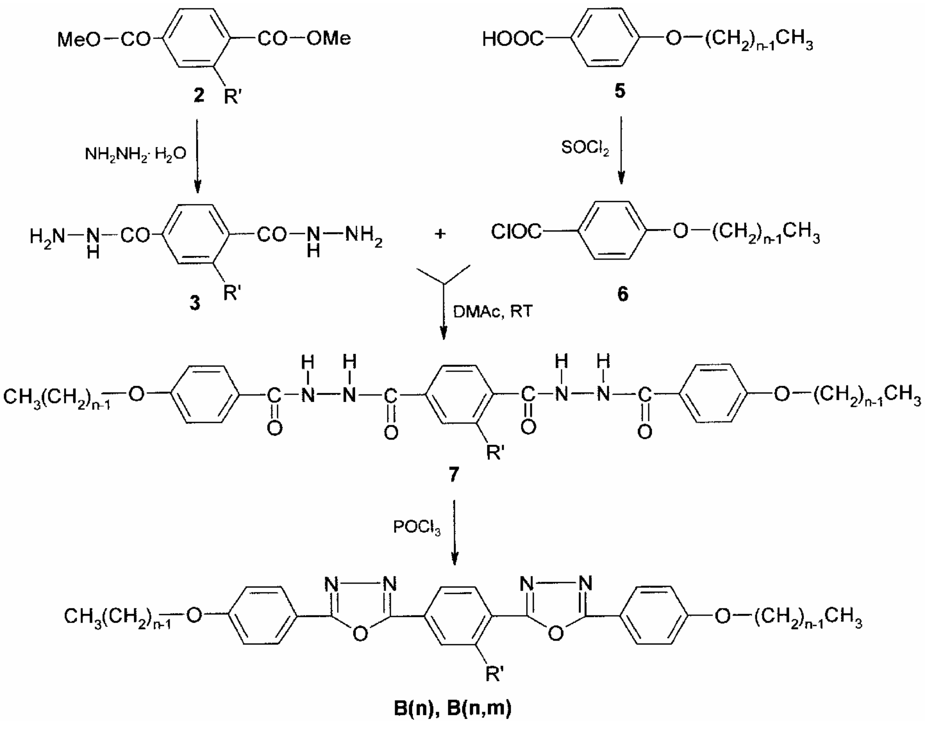
Procedure I (scheme 1). A mixture of the appropriate terephthalic dihydrazide **3** (0.0154 mol) and 4-*n*-alkoxy-benzoic acid **5** (0.0308 mol) in phosphorous oxychloride (70 ml) was heated under reflux for 5 h. The clear solution was cooled and added into water (500 ml) mixed with crushed ice and potassium hydrogen carbonate. The precipitate **B**(***n***) or **B**(***n***,***m***) was filtered and washed with water, dried, purified by crystallization from chloroform, DMF, or tetrahydrofuran (THF) and characterized (see table 1).

Procedure II (scheme 2). To a suspension of terephthalic dihydrazide **3** (1 g, 5.15×10^{-3} mol) in dry *N*,*N*-dimethylacetamide (80 ml) at 0°C, the appropriate *n*-alkoxybenzoic chloride **6** (0.0113 mol, 2:1 + 20% excess) was added dropwise and the reaction was allowed to take place at room temperature overnight. The reaction mixture was then poured into cold water and the resulting solid product filtered and washed twice with water. The resulting azide **7** was collected with a final yield of 58–60%, purified by washing in boiling ethanol and used in the subsequent intramolecular cyclization reaction.

The freshly synthesized azide **7** (1.3 g, 1.85×10^{-3} mol) was poured in 30 ml of phosphorous oxychloride (POCl$_3$); after 1 h the solution became clear and the reaction was



Scheme 1.



Scheme 2.

continued at reflux for 2 h. The clear solution was cooled and added to water (500 ml) with crushed ice and potassium hydrogen carbonate. The precipitate **B**(*n*) or **B**(*n*,*m*) was filtered and washed with water, dried, purified by crystallization from chloroform or DMF and characterized.

Compound **B**(5) was prepared according to procedure I and recrystallized from DMF. The final yield was 20%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.29 (s, 4H); 8.09 (d, 4H); 7.04 (d, 4H); 4.05 (t, 4H); 1.83 (m, 4H); 1.50–1.25 (m, 8H); 0.95 (t, 6H).

B(8) was prepared according to procedure I and recrystallized from DMF; yield 41%. ^{1}H NMR (deuteriated pyridine (Py-d_5)): δ (ppm) = 8.42 (s, 4H); 8.30 (d, 4H); 7.27 (d, 4H); 4.17 (t, 4H); 1.89 (m, 4H); 1.59 (m, 4H); 1.40 (m, 16H); 1.00 (t, 6H).

B(10) was prepared according to procedure II and recrystallized from chloroform; yield 45%. ^{1}H NMR

Table 1. Calorimetric data for **B**(***n***) and **B**(***m,n***) compounds. T_m = melting temperature; ΔH_m = melting enthalpy; T_{is} = isotropization temperature; ΔH_{is} = isotropization enthalpy; T_{an} = isotropic–LC2 transition temperature; ΔH_{an} = isotropic–LC2 enthalpy; solid-solid transition. Data in parentheses refer to the LC2–isotropic phase transition on heating and cooling (see text). For **B**(**10**,**1**) and **B**(**12**,**1**) the monotropic liquid crystalline phase is a nematic. The **B**(**10**,**1**) isotropic liquid-to-nematic transition enthalpy has been evaluated by deconvolving the isotropic–nematic–crystal peak (see figure 8).

Compound	$T_m/°C$	$\Delta H_m/J\,g^{-1}$	$T_{is}/°C$	$\Delta H_{is}/J\,g^{-1}$	$T_{an}/°C$	$\Delta H_{an}/J\,g^{-1}$
B(**5**)	253.6	133				
B(**8**)	172.7	42	237.0	78		
			(231.4)	(56)	(226.6)	(− 58)
B(**10**)	170.0	56	229.0	66		
			(222.0)	(51)	(217.3)	(− 51)
B(**12**)	140.7	10	224.7	75		
			(217.0)	(56)	(212.0)	(− 57)
B(**14**)	135.7	9	215.3	46		
			(206.7)	(34)	(202.6)	(− 32)
B(**10**,**1**)	136.0	7[a]			(149.0)	(− 24)
	164.0	66				
B(**10**,**5**)	161.0	69				
B(**10**,**9**)	154.0	41				
B(**12**,**1**)	120.4	13[a]	(154.7)	(15)	(151.3)	(− 15)
	158.3	64				
B(**N**)	288.0	101				

[a] Solid–solid transition.

($CDCl_3$): δ (ppm) = 8.26 (s, 4H); 8.06 (d, 4H); 7.01 (d, 4H); 4.02 (t, 4H); 1.82 (m, 4H); 1.53 (m, 4H); 1.26 (m, 24H); 0.85 (t, 6H).

B(**12**) was prepared according to procedure II and recrystallized from DMF; yield 40%. ^{1}H NMR (Py-d_5): δ (ppm) = 8.38 (s, 4H); 8.30 (d, 4H); 7.24 (d, 4H); 4.14 (t, 4H); 1.88 (m, 4H); 1.57 (m, 4H); 1.38 (m, 32H); 0.94 (t, 6H).

B(**14**) was prepared according to procedure II and recrystallized from chloroform; yield 35%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.29 (s, 4H); 8.09 (d, 4H); 7.04 (d, 4H); 4.04 (t, 4H); 1.83 (m, 4H); 1.48 (m, 4H); 1.26 (m, 40H); 0.88 (t, 6H).

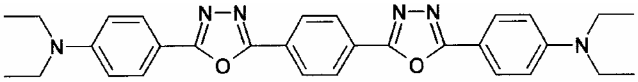
B(**10**,**1**) was prepared according to procedure II and recrystallized from chloroform; yield 19%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.20 (d, 1H); 8.10 (dd, 4H); 7.87 (s, 1H); 7.81 (d, 1H); 7.04 (dd, 4H); 4.15 (s, 3H); 4.05 (t, 4H); 1.84 (m, 4H); 1.48 (m, 4H); 1.36–1.26 (m, 24H); 0.90 (t, 6H).

B(**10**,**5**) was prepared according to procedure I and recrystallized from chloroform; yield 22%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.25 (d, 1H); 8.07 (dd, 4H); 7.82 (s, 1H); 7.75 (d, 1H); 7.03 (dd, 4H); 4.26 (t, 2H); 4.04 (t, 4H); 1.97 (m, 2H); 1.83 (m, 4H); 1.59 (m, 2H); 1.47 (m, 4H); 1.29 (m, 26H); 0.95 (t, 3H); 0.89 (t, 6H).

B(**10**,**9**) was prepared according to procedure I and recrystallized from chloroform; yield 20%. ^{1}H NMR ($CDCl_3$): δ (ppm) = 8.26 (d, 1H); 8.09 (dd, 4H); 7.84 (s, 1H); 7.77 (d, 1H); 7.03 (dd, 4H); 4.26 (t, 2H); 4.04 (t, 4H); 1.97 (m, 2H); 1.83 (m, 4H); 1.59 (m, 2H); 1.48 (m, 4H); 1.28 (m, 34H); 0.87 (m, 9H).

B(**12**,**1**) was prepared according to procedure I and recrystallized from DMF/water; yield 20%. ^{1}H NMR (Py-d_5): δ (ppm) = 8.40 (d, 1H); 8.31 (dd, 4H); 8.03 (s, 1H); 7.98 (d, 1H); 7.25 (dd, 4H); 4.05 (m, 4H); 4.02 (s, 3H); 1.82 (m, 4H); 1.47 (m, 4H); 1.28 (m, 32H); 0.89 (t, 6H).

Compound **B**(**N**) has the structure:

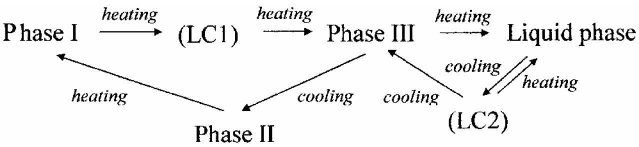


A mixture of terephthalic dihydrazide (5.15×10^{-3} mol) and *N*,*N*-diethylaminobenzoic acid (0.0113 mol) in phosphorous oxychloride (70 ml) was heated at reflux for 4 h. The excess of phosphorous oxychloride was distilled off under reduced pressure and the product obtained was poured into aqueous NaOH (0.1M, 500 ml). The precipitate was filtered and washed with water, dried, purified by crystallization from THF/water and characterized; yield 18%. ^{1}H NMR (DMSO-d_6): δ (ppm) = 7.95 (s, 4H); 7.65 (d, 4H); 6.55 (d, 4H); 3.23 (q, 8H); 1.01 (t, 12H).

3. Results and discussion

3.1. *Phase behaviour*

Calorimetric data for the synthesized compounds are given in table 1. The DSC traces of **B**(**10**), are representative of those for the **B**(***n***) series, and are shown in figure 1. A summary of the phase transitions seen for **B**(**10**), is given in scheme 3.



Scheme 3.

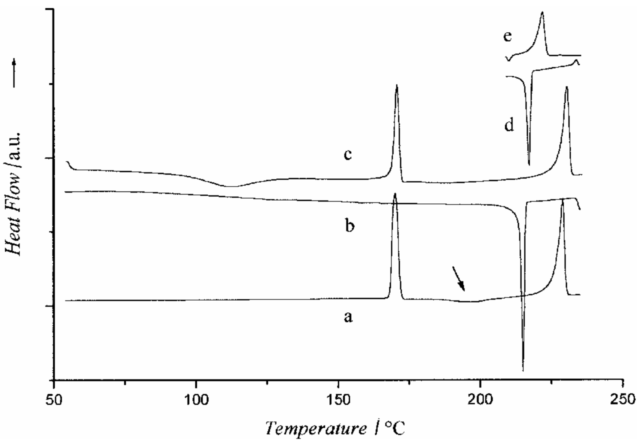


Figure 1. DSC traces of **B**(**10**): (*a*) first heating run; (*b*) first cooling run; (*c*) second heating run; (*d*, *e*) cooling run and subsequent fast heating run for isolating the monotropic LC2–isotropic liquid transition.

At room temperature **B**(**10**) shows two crystalline phases, one obtained by crystallization from chloroform solution, denoted phase I (i.e. virgin samples as obtained from the synthesis), and the other, denoted phase II, obtained by crystallization from the melt. On heating, phase II undergoes a transition to phase I accompanied by a small exothermic peak at about 113°C, figure 1 (*c*). The XRD patterns of the two crystalline phases are characterized by several very sharp diffraction rings, with the most intense reflection located at low angle, see tables 2 and 3, and figures 2 (*a*) and 2 (*b*).

The dependence of the low angle d-spacing on n is shown in figure 3: it is evident that a layered packing occurs only for $n = 12$, 14, phase I, and for $n = 8$–14, phase II. The molecular lengths, evaluated for the most extended conformation and using standard bond lengths and bond angles, is also shown in figure 3 and these are larger than the layer thicknesses. This may be explained by a perpendicular arrangement of the molecules with respect to the layer plane, but with interpenetrating aliphatic tails, by non-extended conformations, or by molecules being in their most extended conformations but tilted with respect to the layer plane. For $n = 12$, 14, the low angle d-spacing of phases I and II is the same, suggesting the occurrence of a very similar layered molecular packing.

Table 2. d-Spacings and relative intensities (based on visual inspection) for phases exhibited by **B**(**10**).

Phase I		Phase II		Phase III	
d/Å	Intensity[a]	d/Å	Intensity[a]	d/Å	Intensity[a]
14.7	vvs	32.0	vvs	33.2	vvs
7.11	vvw	7.96	vvw	8.22	vvw
5.59	vw	6.06	s	6.10	s
5.25	vvw	5.48	vvw		
4.93	m	5.04	m	5.30	vvw (broad)
4.28	vvw	4.63	w		
3.94	vw	4.21	w	4.36	vvw (broad)
3.69	s	4.03	vvw		
3.53	s	3.47	vvw		
3.21	w	3.22	vvw		
3.12	w				

[a] vvs = very very strong; s = strong; m = medium; w = weak; vw = very weak; vvw = very very weak.

Table 3. d-Spacings of the low angle reflections for phases I and II measured at room temperature.

Compound	d/Å (phase I)	d/Å (phase II)	Calculated length/Å
B(**5**)	10.2	6.1	32.4
B(**8**)	13.5	28.8	39.9
B(**10**)	14.8	32.0	44.9
B(**10**,**1**)	n.o.[a]	30.8	44.9
B(**12**)	34.6	35.4	49.9
B(**12**,**1**)	n.o.[a]	33.3	49.9
B(**14**)	38.6	39.0	54.9

[a] New layered phase is observed at room temperature for **B**(**10**,**1**) and **B**(**12**,**1**) with diffraction pattern only slightly different from that of phase II.

At high temperature, **B**(**10**) exhibits complex behaviour. As observed by optical microscopy, phase I melts to a fluid anisotropic liquid phase and then undergoes an abrupt transformation into a non-fluid phase. This corresponds to the small and broad exothermic transition seen in figure 1 (*a*) at about 195°C (indicated by an arrow). These changes might be explained by the melting of phase I into a liquid crystalline (LC) phase, denoted LC1, and a subsequent spontaneous transition into a more stable non-fluid phase, denoted phase III. The characterization of the LC1 phase using XRD was not possible because it was observed only for an extremely short time prior to the transition into phase III (a few seconds). The XRD pattern of phase III, taken at 210°C and shown in figure 4, is similar to that of phase II, with the same d-spacing at low angle reflection. The diffraction intensities of these two phases are compared in figure 5.

When the sample of **B**(**10**) is heated to the isotropization temperature, figure 1 (*c*), and subsequently cooled to the anisotropic phase, 1 (*d*), two different transition enthalpies are measured (table 1). Specifically the enthalpy measured on cooling is smaller. We suggest

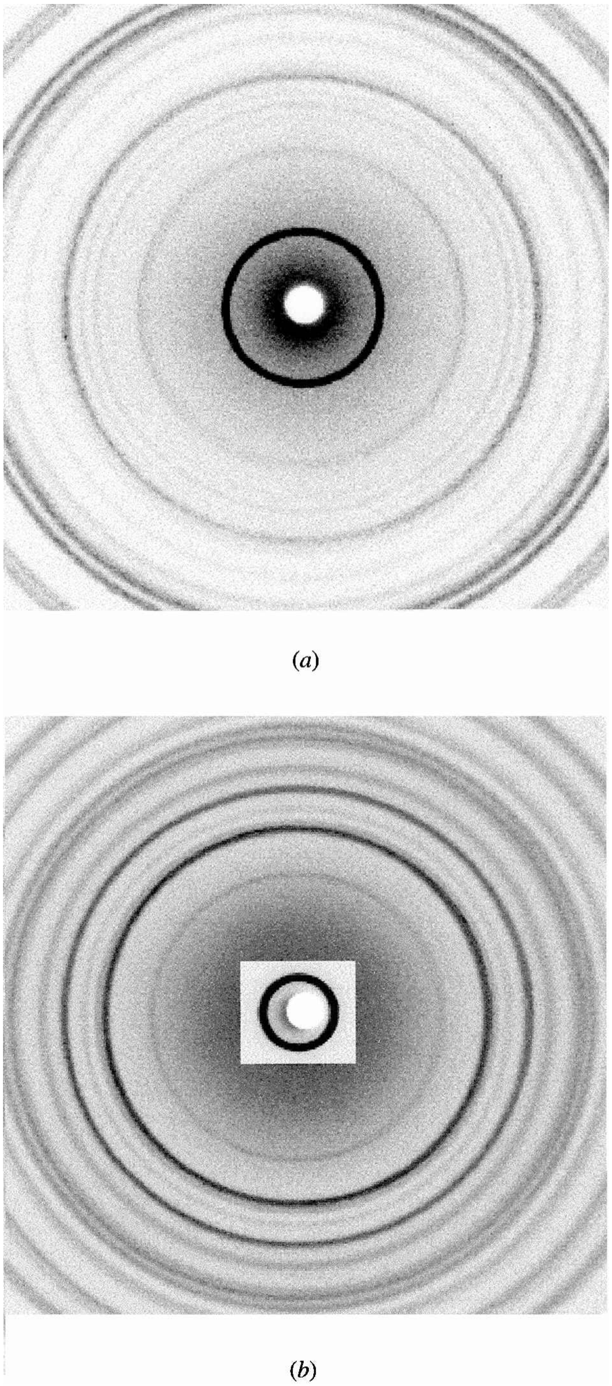
Table 4. Optical characterization data of the synthesized compounds.

Compound	λ_{max} abs.[a]/nm (ε)/M^{-1} cm^{-1}	λ_{max} em.[b]/nm
B(**5**)	337 (52000)	418
B(**8**)	337 (51000)	419
B(**10**)	339 (49800)	418
B(**12**)	339 (47500)	418
B(**14**)	334 (50000)[c]	418
B(**10**,**1**)	344 (43000)	410
B(**10**,**5**)	344 (45000)	409
B(**10**,**9**)	338 (41000)	408
B(**12**,**1**)	343 (51500)	410
B(**N**)	383 (53000)	570

[a] Wavelength at the absorption maximum.
[b] Wavelength at the luminescent emission maximum, DMF solutions.
[c] Measured in chloroform solution.

that this smaller value indicates the appearance of a new phase on cooling, which is different from and unstable with respect to phase III. A subsequent fast heating ramp can be used to measure the transitional data of this new phase, figure 1 (*e*). Now, the enthalpies measured on heating and cooling are equal (table 1). As observed by microscopy, on cooling a smectic-type texture appears, which suddenly changes to a more structured texture. All those features, including just a few degrees of undercooling for the transition, support the LC nature of this new phase, which is denoted LC2. This is also consistent with the optical texture taken at 210°C and shown in figure 6 (*a*).

In addition, phase III can be regarded as a highly ordered smectic phase or a disordered crystal [46, 47] see figure 6 (*b*); in fact the XRD pattern recorded at 210°C (figure 4) shows only a few diffraction rings. Whilst the low angle d-spacing corresponds to the layer periodicity (reflection with Bragg indices 0 0 1), the strong reflection with d-spacing 6.10 Å may correspond to the superimposed reflections with Bragg indices 1 1 0 and 2 0 0 in the case of a pseudo-hexagonal molecular packing (herringbone fashion). This packing is compatible with the flat shape of the aromatic segment (fact-to-edge packing) as frequently observed for substituted oxadiazole systems [48–51] and for analogous compounds [52]. Accordingly, a rectangular unit cell with cell parameters $a = 12.20$ Å and $b = 7.04$ Å can be assigned.


(*a*)

(*b*)

Figure 2. XRD patterns of **B**(**10**): (*a*) crystalline phase I; (*b*) crystalline phase II.

The thermal behaviour of **B**(***n***,***m***) is different. In the calorimetric traces, **B**(**10**,**5**) and **B**(**10**,**9**) show only a melting transition at 161 and 156°C, respectively (table 1). Compared with **B**(**10**), the isotropic liquid phase is obtained at temperatures lower by about 60 and 85°C, respectively, showing that side groups strongly affect molecular packing and destabilize the smectic

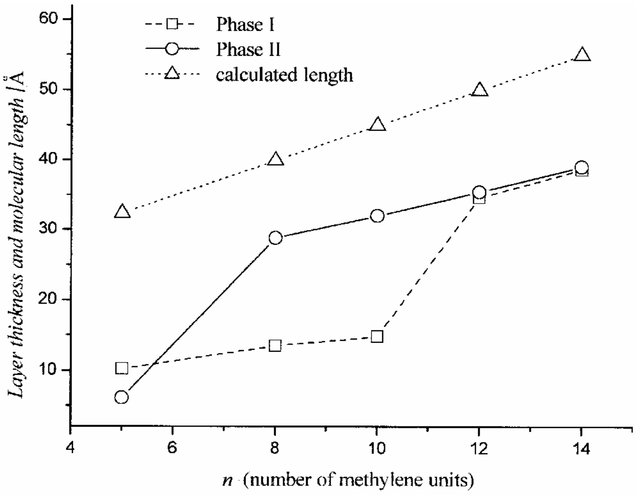


Figure 3. Low angle d-spacing of phases I and II seen for **B**(n) as a function of n, the number of methylene units.

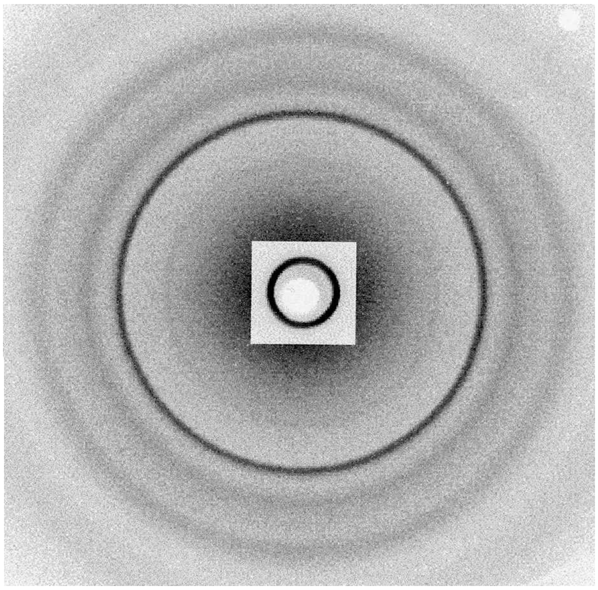


Figure 4. XRD pattern of **B**(**10**) crystalline phase III at 210°C.

order. The shorter methoxy unit of **B**(**10**,**1**) and **B**(**12**,**1**), whilst similarly destabilizing smectic order, is essentially ineffective in modifying the melting temperature and promotes the formation of a monotropic nematic phase (see optical texture and DSC traces in figures 7, 8 and 9).

In the case of **B**(**10**,**1**), the nematic–isotropic peak cannot be isolated in the calorimetric analysis, because of the fast crystallization process. Thus, the associated enthalpy can only be evaluated by the deconvolution of the whole isotropic–nematic–crystal peak (figure 8). For **B**(**12**,**1**), the nematic–isotropic transition can be easily isolated (figure 9) and the associated enthalpy directly evaluated.

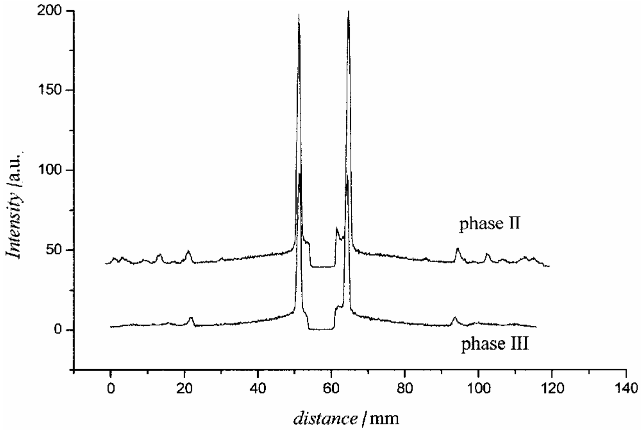


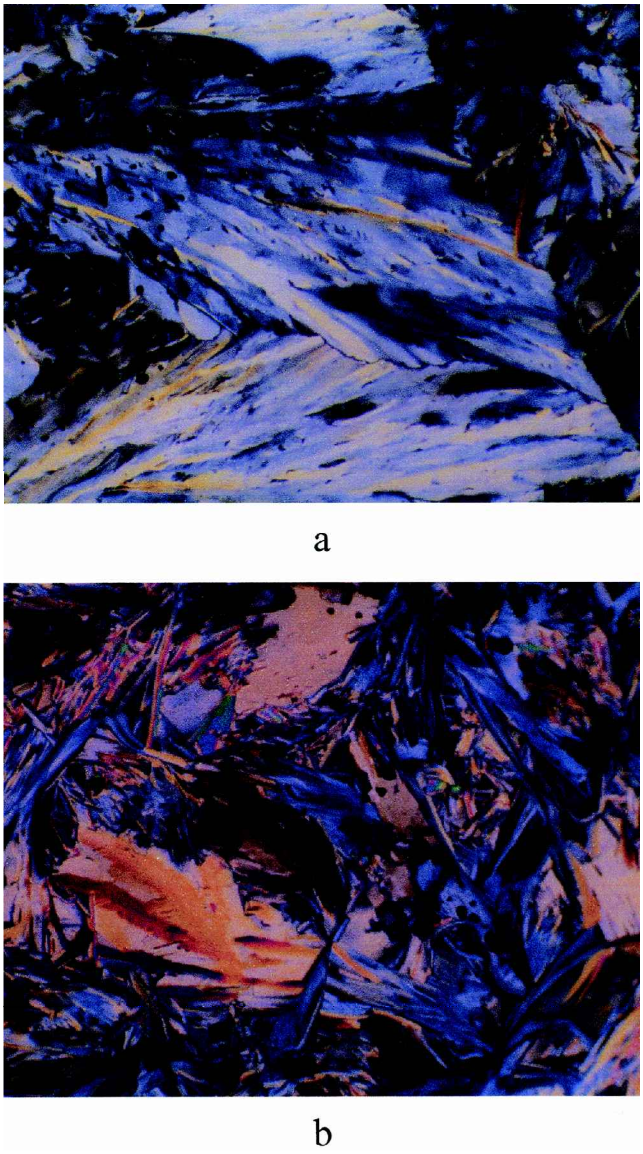
Figure 5. XRD scan (powder spectra) of **B**(**10**) for phase II, figure 2(b), and phase III, figure 4.

3.2. *Optical properties*

All the synthesized compounds were analysed by UV-vis and fluorescence spectroscopy in diluted solutions. The optical absorption and emission maxima as well as the extinction coefficients are reported in table 1. Data were recorded in DMF solutions, except for **B**(**14**) which is much more soluble in chloroform. **B**(n) compounds show an absorption band centred around 340 nm. **B**(n,m) show two absorption bands at around 320 and 340 nm, probably corresponding to the absorption of a single alkoxyphenyl ring and of the whole conjugated system, respectively. **B**(**n**) shows a red-shift of the maximum absorption wavelength at around 380 nm. This bathochromic shift can be ascribed to the presence of the strong electron-donating amino groups, which decrease the gap between the energy of the ground state and the first excited state, shifting the absorption to higher wavelengths. Photoluminescence spectra were also obtained on the same solutions excited at the wavelength of maximum absorption: for **B**(n) and **B**(n,m) compounds there is a maximum emission band in the violet–blue region, at around 410–420 nm, for **B**(**N**) the emission band peak is shifted to the yellow region, at around 570 nm. The striking similarity of the UV-vis and fluorescence spectra in solution suggests that the molecular photo-physical properties of these compounds are predominantly governed, as expected, by the rigid conjugated moiety and are not strongly influenced by the insertion or the length of the alkoxy side group. All the solutions are transparent at wavelengths longer than 520 nm. Figure 10 shows the absorption and the emission spectra of **B**(**10**) in DMF as a representative example.

4. Conclusions

We found that 1,4-bis(5-phenyl-1,3,4-oxadiazolyl)-benzene-containing compounds possess good fluorescence properties. A smectic type packing, observed at high



a

b

Figure 6. Optical textures of **B**(**10**) captured during a fast cooling run at 220°C: (*a*) the unstable LC2 phase; (*b*) the stable phase III, according to scheme 3. Crossed polarizers, ×20.

temperatures for some of the synthesized compounds, is favoured by the conjugated structure of the 1,4-bis-(5-phenyl-1,3,4-oxadiazolyl)benzene unit. The lateral aliphatic group strongly destabilizes the smectic phase which disappears completely for **B**(**10**,***m***) even in the case of the shortest methoxy unit ($m = 1$). On the other hand, the crystalline phase is only slightly destabilized. For example, the melting temperature decreases by only 16°C going from **B**(**10**) to **B**(**10**,**9**). A nematic phase is observed for **B**(**10**,**1**) and **B**(**12**,**1**), showing that the length of the lateral substituent plays a role in promoting nematic order.

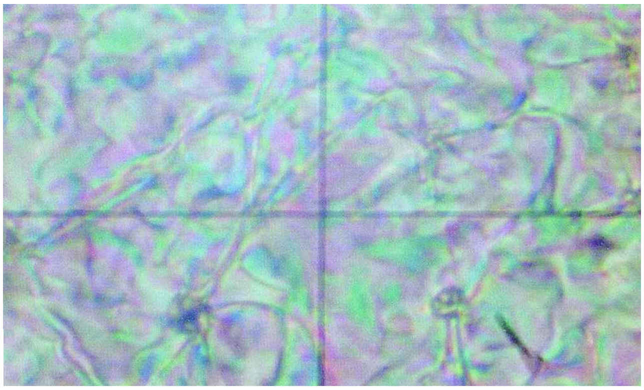


Figure 7. Nematic marbled texture of **B**(**10**,**1**) taken at 145°C during the cooling run. Crossed polarizers, ×20.

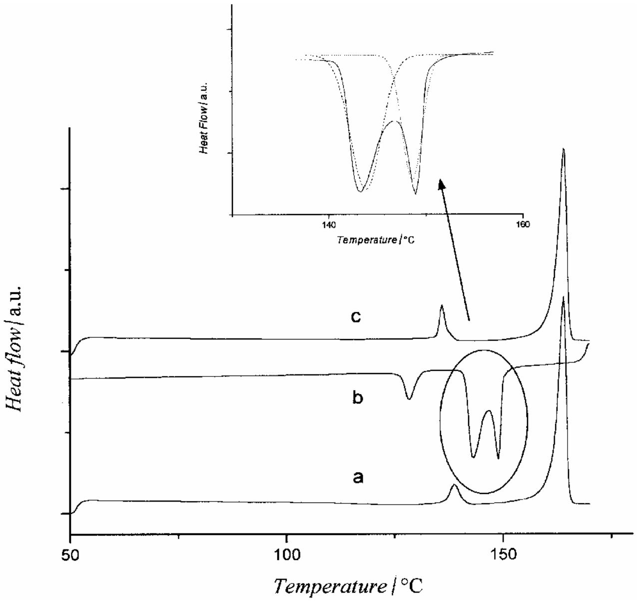


Figure 8. DSC traces of **B**(**10**,**1**): (*a*) first heating run; (*b*) first cooling run; (*c*) second heating run. The isotropic–nematic–crystal peak is shown by an arrow.

The mesogenic character of this unit may be of interest in the synthesis of liquid crystalline polymeric systems, taking advantage of both the optical properties and the peculiar organization of molecules in the liquid crystalline state. The synthesis of segmented polymers and copolymers with the same monomeric unit investigated in this paper is now under scrutiny. Moreover the effect of electron-accepting and electron-donating groups on the fluorescence properties and on the formation of liquid crystalline phases of this family of compounds is at present under investigation.

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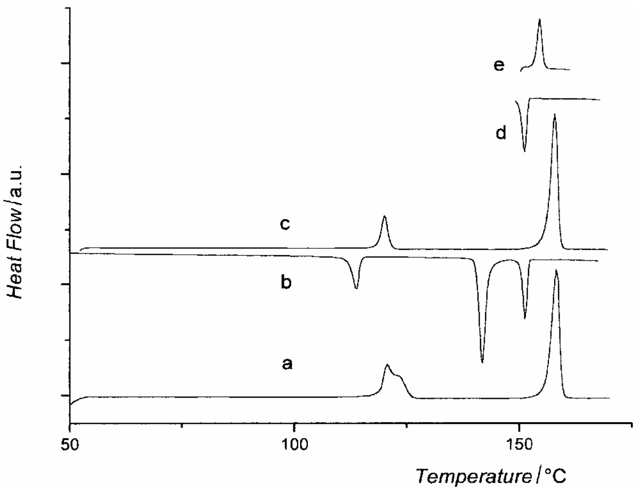

Figure 9. DSC traces of **B**(**12**,**1**): (*a*) first heating run; (*b*) first cooling run; (*c*) second heating run; (*d*, *e*) nematic–isotropic and isotropic–nematic peaks have been isolated.

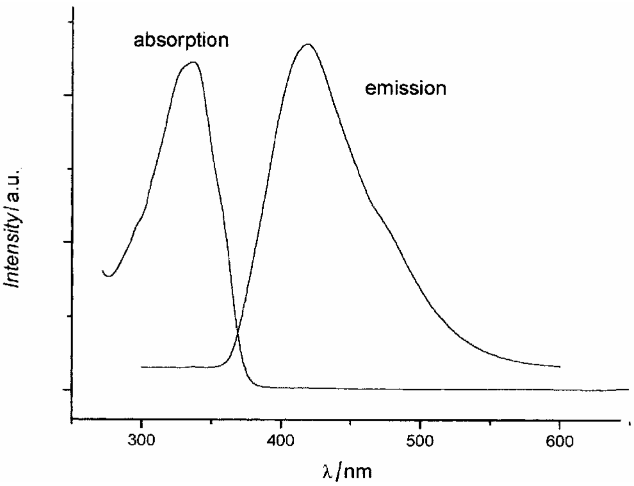

Figure 10. Absorption and emission spectra of **B**(**10**) in DMF solution.

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