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## Liquid Crystals

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### Mesogenic behaviour in some pyrazole and isoxazole derivatives

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## Mesogenic behaviour in some pyrazole and isoxazole derivatives

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Several aromatic  $\beta$ -diketones with a different number of alkyloxy groups in the aromatic rings and their derived pyrazoles, isoxazoles and thallium (I) complexes have been synthesized. The potential mesomorphic properties of these compounds have been investigated by optical microscopy, DSC and X-ray diffraction. The pyrazoles and isoxazoles with one chain in each aromatic ring are mesogenic, showing smectic A and smectic C mesophases, whereas the pyrazoles and isoxazoles with two chains per ring and the  $\beta$ -diketones and thallium complexes are not. The mesogenic potentiality is shown to be related to the molecular linearity and to the number of alkyloxy groups. To the best of our knowledge, this is the first time liquid crystal properties have been described for pyrazole and isoxazole derivatives.

### 1. Introduction

This work deals with the potential mesomorphic properties of some  $\beta$ -diketones and their derivatives. The 4-alkyl- or 4-alkyloxy-substituted aromatic  $\beta$ -diketones and their copper complexes have been reported as mesomorphic [1-4]; the type of mesophase depends on the nature and length of the terminal chain. It has been shown that the short chains give rise to rather narrow mesophase ranges or no mesophases at all; therefore the intermediate and long chains are of greater interest.

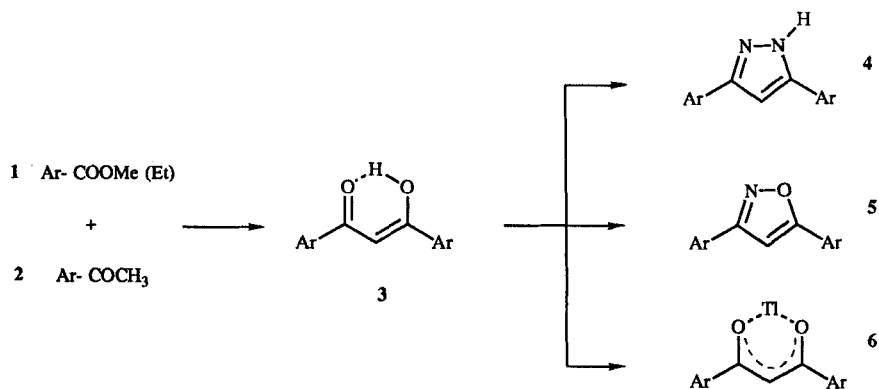
In this work we aim to widen our knowledge about the mesogenic properties of the 4-alkyloxy-substituted aromatic  $\beta$ -diketones and some of their derivatives. In particular, we have investigated the potential mesomorphism of three novel kinds of  $\beta$ -diketone derivatives: pyrazoles and isoxazoles, derived from the reaction of  $\beta$ -diketone with hydrazine and hydroxylamine respectively, and a thallium complex obtained by the reaction of the  $\beta$ -diketone with thallium ethoxide. As  $\beta$ -diketones we have used 1,3-di(4-*n*-octyloxyphenyl)propane-1,3-dione and 1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dione. The corresponding pyrazoles and isoxazoles of both  $\beta$ -diketones and the thallium complex of the decyloxy-substituted  $\beta$ -diketone have been prepared and their mesomorphic behaviour investigated.

### 2. Results and discussion

#### 2.1. Mesomorphic properties

Ohta and coworkers [2,4] have reported the existence of smectic mesomorphism for the series of 1,3-di(4-*n*-alkoxyphenyl)propane-1,3-diones. In the compounds of this series synthesized by us (**3a** and **3b**, see table 1) we observed a phase transition before melting to the isotropic liquid. Under the polarizing microscope this transition was

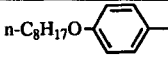
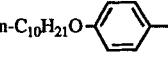
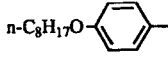
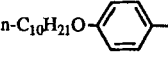
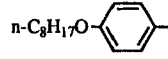
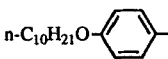
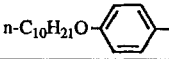
\* Author for correspondence.



observed as a subtle change to an uncharacteristic texture, and the sample could not be made to flow by slipping the cover over the slide. With DSC the highest temperature peak, corresponding to the isotropic liquid transition (85.3°C,  $\Delta H = 27.3 \text{ kJ mol}^{-1}$  for **3a** and 92.6°C,  $\Delta H = 48.7 \text{ kJ mol}^{-1}$  for **3b**, see table 1), considerably supercools on the cooling scans (transition at 71.2°C for **3a** and 72.9°C for **3b** at  $10^\circ \text{ min}^{-1}$ ). These data agree with the  $C_2$  phase being a crystal or a crystalline smectic phase.

The two pyrazoles (**4a** and **4b**) exhibit four transitions on heating and on cooling under the microscope as well as with DSC (see table 1). Under the polarizing microscope on heating the crystal phase there is a transition, corresponding to the first DSC peak, to a phase with a mosaic texture that might be another crystal phase or an

Table 1. Optical, thermal and thermodynamic data for the 1,3-di(4-*n*-alkoxyphenyl)propane-1,3-diones and derivatives.

Compound	Ar	Transition	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
<b>3a</b>		C <sub>1</sub> -C <sub>2</sub>	78.1	6.5
		C <sub>2</sub> -I	85.3	27.3
<b>3b</b>		C <sub>1</sub> -C <sub>2</sub>	62.5	23.17
		C <sub>2</sub> -I	92.6	48.7
<b>4a</b>		C <sub>1</sub> -C <sub>2</sub>	61.7	26.9
		C <sub>2</sub> -S <sub>C</sub>	143.3	14.3
		S <sub>C</sub> -S <sub>A</sub>	179.4	0.3
		S <sub>A</sub> -I	192.2	6.4
<b>4b</b>		C <sub>1</sub> -C <sub>2</sub>	79.3	31.8
		C <sub>2</sub> -S <sub>C</sub>	130.3	13.1
		S <sub>C</sub> -S <sub>A</sub>	180.5	0.3
		S <sub>A</sub> -I	182.9	6.1
<b>5a</b>		C <sub>1</sub> -S <sub>C</sub>	75.8	17.8
		C <sub>2</sub> -S <sub>C</sub>	94.5	14.1
		S <sub>C</sub> -I	132.7	2.0
<b>5b</b>		C <sub>1</sub> -S <sub>C</sub>	95.1	56.4
		C <sub>2</sub> -S <sub>C</sub>	98.6	
		S <sub>C</sub> -I	147.4	7.7
<b>6b</b>		C-I	85.0	53.5

ordered smectic phase. The phase undergoes a transition, corresponding to the second DSC peak, to a fluid birefringent phase showing the typical textures of a smectic C mesophase. At a higher temperature a new transition occurs, corresponding to the third DSC peak, to another mesophase easily identifiable by its textures as smectic A. Finally the  $S_A$  mesophase transforms into the isotropic liquid at a temperature that corresponds to the highest temperature DSC peak. The two highest temperature DSC peaks ( $S_C$ - $S_A$  and  $S_A$ -I transitions) are found at the same temperatures in the heating and in the cooling scans. The peak corresponding to the transition between the unknown phase and the  $S_C$  phase is observed at a temperature about 7° lower for the cooling than for the heating processes. On the other hand the lowest temperature transition supercools considerably.

The two isoxazoles (**5a** and **5b**) investigated show mesogenic properties. Under the polarizing microscope on heating we observed in both cases a transition from the solid to a mesophase identified as smectic C by its optical textures. If we go on heating the sample, it becomes isotropic. In DSC we find two or more endotherms in all the scans at relatively low temperatures, of which the one which appears at the highest temperature corresponds to the crystal-mesophase transition observed by microscopy. The other peaks result from double melting phenomena or crystal-crystal transitions. In addition to this, another endotherm at higher temperatures is observed for both compounds, corresponding to the mesophase-isotropic liquid transitions.

[1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dionate] thallium(I) (**6b**) is not mesogenic; the solid melts directly to the isotropic liquid at 85.0°C.

## 2.2. X-ray study

In order to verify the nature of the mesophases of these compounds we have performed X-ray diffraction experiments on the magnetically aligned mesophases of the decyloxy-substituted pyrazole (**4b**), as well as on the unidentified phase that appears between 79.3°C and 130.3°C in this compound. Several diffraction patterns for the  $S_A$  and  $S_C$  phases were recorded at different temperatures starting from the  $S_A$  phase. All of them consist, as generally happens with  $S_A$  and  $S_C$  mesophases, of two regions. The first is a sharp reflection at small angles in the meridian region (parallel to the alignment direction). This small angle maximum gives the interlayer spacing (see table 2). The second is a diffuse ring split into two crescents concentrated in the equator (perpendicular to the alignment direction). It corresponds to a distance of 4.5–4.6 Å and is associated with the aliphatic chain interferences.

From the interlayer distances listed in table 2 for the  $S_A$  and  $S_C$  mesophases, a tilt angle of 23° is estimated for the  $S_C$  mesophase. This value does not change significantly with temperature, except close to the transition to the  $S_A$  mesophase.

Table 2. Measured distances by X-ray diffraction in compound **4b**.

$T/^\circ\text{C}$	Phase	Layer spacing/Å	Tilt angle/ $^\circ$
182	$S_A$	34.7	—
180	$S_C$ - $S_A$ transition	34.7	—
178	$S_C$	33.1	17
165	$S_C$	32.0	23
152	$S_C$	32.0	23
140	$S_C$	32.0	23

On cooling the  $S_C$  mesophase in the magnetic field into the unidentified phase, a pattern is obtained that partially maintains the orientation of the  $S_A$  and  $S_C$  patterns. At small angles a set of sharp reflections are observed with a distance ratio of 1:1/2:1/3:1/4... typical of a lamellar structure. At middle and wide angles a complicated pattern is obtained with a great number of sharp reflections, which suggests that we are dealing with a three dimensional crystal rather than a mesophase. The measured periodicity of this lamellar crystal is 32.4 Å which is lower than the periodicity of the  $S_A$  phase, and so indicates that the molecules are tilted.

### 2.3. Structure-mesomorphism relationship

In order to understand better why the pyrazole and isoxazole derivatives are mesogenic, while the  $\beta$ -diketones and the thallium complex are not, we must remember that the most favourable geometry for a molecule showing calamitic mesophases is linear. All of the molecules described in this paper have a non-linear core, the deviation from linearity being variable depending on the type of compound.

The diffraction data of other, similar  $\beta$ -diketones [5, 6], isoxazoles [7] and thallium complex [8] taken from the literature are gathered in figures 1 (a), (b) and (c). From figure 1 it can be deduced that the isoxazole molecules do not deviate significantly from linearity. On the other hand the  $\beta$ -diketone and the thallium complex have a bent geometry, which prevents these molecules from being mesomorphic. AM1 [9] and CNDO/2 calculations carried out by us indicate the practically linear geometry of the pyrazole compounds, for which diffraction data have not been found in the literature. Figures 1 (d) and (e) result from our calculations.

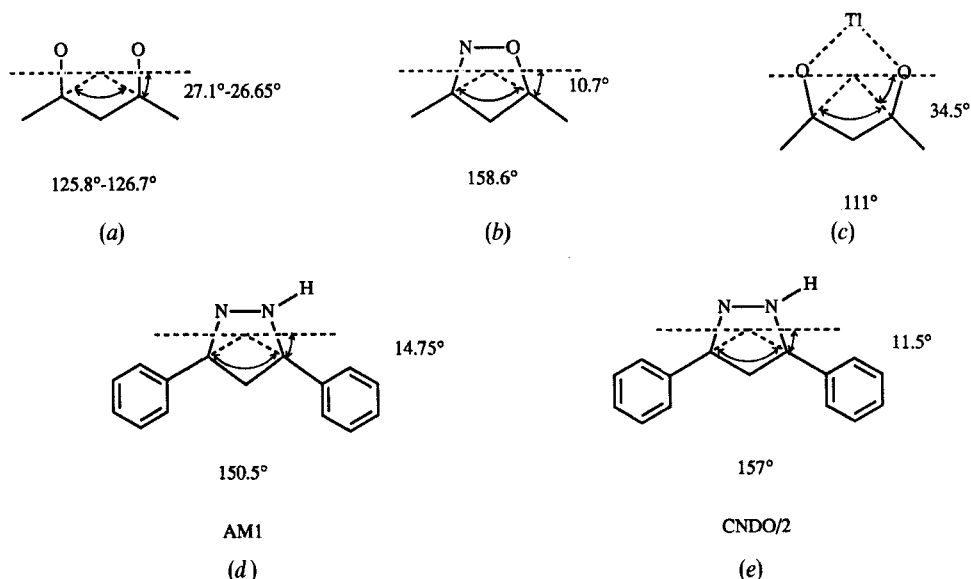


Figure 1. Deviation from linearity of 1,3-disubstituted propane-1,3-diketones and derivatives, (a) 1,3-diphenylpropane-1,3-dione, (b) 3,5-diphenyl isoxazole, (c) 1,3-bis-(tri-fluoromethyl)propane-1,3-dionate thallium(I), (d) 3,5-diphenyl pyrazole, calculated by the AM1 method, (e) 3,5-diphenyl pyrazole, calculated by the CNDO/2 method.

#### 2.4. Hydrogen bonding in the pyrazoles

The existence of intermolecular hydrogen bonds in the pyrazole derivatives might play a fundamental role, as they make the appearance of dimers possible (see figure 2). The similarity of the properties of the pyrazoles and isoxazoles suggest that this effect is not significant. However, with the aim of assessing the importance of hydrogen bonding we have made a variable temperature infrared spectroscopic study of compounds **4a** and **4b**. In figure 3 the nitrogen–hydrogen stretching vibration of compound 3,5-di(4-*n*-decyloxyphenyl)pyrazole (**4b**) in the different phases on heating from the crystal to the isotropic liquid and on cooling from the isotropic liquid to the crystal is represented. As can be seen from figure 3(a), the  $C_1$  phase shows at 60°C a single absorption at  $3428.5\text{ cm}^{-1}$ ; this frequency corresponds to the existence of non-associated NH. The spectrum at 98°C ( $C_2$  phase) shows a single band at  $3249.1\text{ cm}^{-1}$  (see figure 3(b)), suggesting an important change in the structure, possibly due to the existence of intermolecular hydrogen bonds. In the spectra of the  $S_C$ ,  $S_A$  and isotropic phases (see figures 3(c), (d) and (e), respectively) there are two bands of similar intensity that correspond to the species with free (*c.*  $3419\text{ cm}^{-1}$ ) and associated (*c.*  $3259\text{ cm}^{-1}$ ) NH bonds. In the cooling process the results obtained are very similar (see figure 3(f) and (g)). However, the room temperature infrared spectrum (see figure 3(h)) shows only associated NH bands, which indicates that either the  $C_2$  phase supercools or a new crystalline phase, different from  $C_1$ , is obtained. The DSC studies support the second hypothesis. The results of the infrared study of compound **4a** are practically identical; two bands of similar intensity that correspond to the species with free (*c.*  $3419\text{ cm}^{-1}$ ) and associated (*c.*  $3238\text{ cm}^{-1}$ ) NH bonds are observed in the spectra of the  $S_C$ ,  $S_A$  and isotropic phases.

The fact that no significant differences are observed between the spectra of the mesophases and of the isotropic liquid suggests that hydrogen bonding does not play a crucial role in the mesomorphic phases. Nevertheless, the existence of intermolecular hydrogen bonds in the mesophase points to the possibility of obtaining discotic mesophases in the pyrazole derivatives if the number of terminal chains in the aromatic rings is increased. With this aim in mind we prepared 1,3-bis(3,4-di-*n*-decyloxyphenyl) and 1,3-bis(3,5-di-*n*-decyloxyphenyl)propane-1,3-diones (**3c** and **3d**, respectively) and their derived pyrazoles (**4c**, **4d**) and isoxazoles (**5c**, **5d**). None of the compounds synthesized (table 3) exhibit mesomorphism (this was expected for the isoxazole derivatives). The increased number of terminal chains disrupts the calamitic mesomorphism, and the existence of hydrogen bonding in the pyrazole derivatives is not important enough to lead to discotic phases.

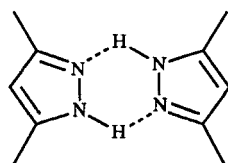


Figure 2. Hydrogen-bonded dimeric pyrazole.

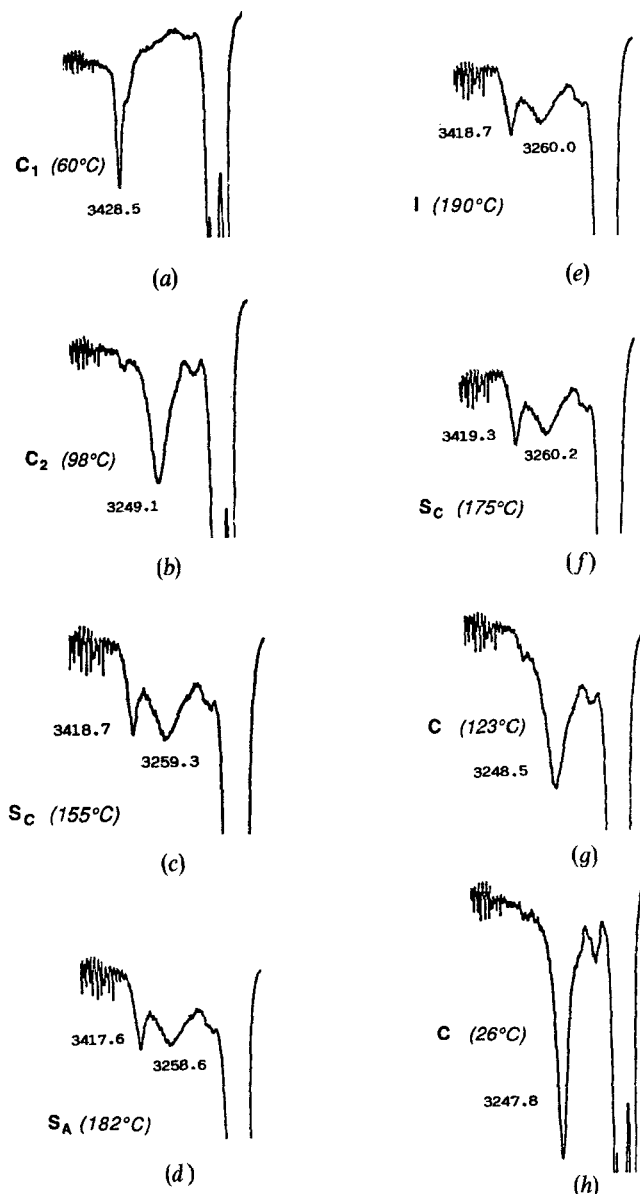


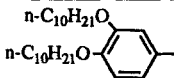
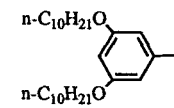
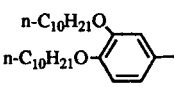
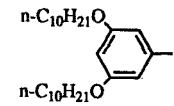
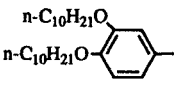
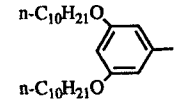
Figure 3. IR spectra showing the nitrogen-hydrogen stretching vibration of compound **4b** at different temperatures.

### 3. Experimental

#### 3.1. General considerations

The compounds have been characterized satisfactorily by <sup>1</sup>H NMR and IR spectroscopy and C,H,N microanalysis. <sup>1</sup>H NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were obtained on a Perkin-Elmer 1600 (series FTIR) spectrometer. Microanalyses were performed with a Perkin-Elmer 240 B microanalyser. The <sup>1</sup>H NMR spectra show that the β-diketones are totally in the enol form. The

Table 3. Optical, thermal and thermodynamic data for the 1,3-bis(3,4 and 3,5-di-*n*-decyloxyphenyl)propane-1,3-diones and derivatives.

Compound	Ar	Transition	$T/^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
3c		C-I	76.6	74.0
3d		C-I	39.2	25.3
4c		C <sub>1</sub> -C <sub>2</sub> C <sub>2</sub> -I	75.6 94.8	37.6 16.4
4d		C-I	58.1	46.26
5c		C-I	91.0	71.6
5d		C-I	46.8	105.9

optical textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and an FP80 central processor. The transition temperatures were measured by differential scanning calorimetry with Perkin-Elmer DSC-2 and DSC-7 instruments operated at a scanning rate of  $10^\circ\text{C min}^{-1}$  on heating. The apparatus were calibrated with indium ( $156.6^\circ\text{C}$ ;  $28.4\text{ J/g}$ ) and tin ( $232.1^\circ\text{C}$ ;  $60.46\text{ J/g}$ ) as standards. X-ray diffraction experiments were carried out at the Laboratoire de Physique des Solides (Université Paris-Sud, Orsay, France). The home-made apparatus uses a monochromatic Cu-K $\alpha$  X-ray beam issued from a double bent pyrolytic graphite monochromator. The samples, held in Lindemann glass tubes ( $\phi = 1.5\text{ mm}$ ), were aligned with a magnetic field-perpendicular to the X-ray beam. The temperature of the sample was constant to within  $\pm 1\text{ K}$ . The diffraction patterns were collected on photographic film.

### 3.2. Synthesis of the $\beta$ -diketones

#### 3.2.1. 1,3-di(4-*n*-octyloxyphenyl)propane-1,3-dione (3a)

A mixture of 20 mmol of ethyl 4-*n*-octyloxybenzoate and 20 mmol of 4-*n*-octyloxyacetophenone in dimethoxyethane was refluxed for 2 hours in the presence of 1.6 g of 60 per cent sodium hydride (40.1 mmol) and then stirred overnight. A small amount of water was added very carefully to the reaction mixture. After acidifying with dilute hydrochloric acid, the product was extracted with ether. Evaporation gave the crude  $\beta$ -diketone 3a which was purified by washing with ethylacetate and then recrystallizing from ethanol. Yield: 82 per cent.



Elemental analysis. Found (calculated for  $C_{31}H_{44}O_4$ ): C 77.53 per cent (77.50 per cent), H 9.71 per cent (9.16 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3397 (OH), 1604 (C=O), 1498 (C=C).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.88 (t, 6 H,  $CH_3$ ), 1.25–1.50 (m, 20 H,  $-[CH_2]_{5-}$ ), 1.80 (m, 4 H,  $-CH_2-[CH_2]_{5-}$ ), 4.02 (t, 4 H,  $-OCH_2$ ), 6.72 (s, 1 H,  $-CH=$ enol), 6.95 (d, 4 H, aromatic- $H_{3,5}$ ), 7.94 (d, 4 H, aromatic- $H_{2,6}$ ), 17.16 (s, 1 H,  $-OH$  enol).

### 3.2.2. 1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dione (3b)

The compound was synthesized from ethyl 4-*n*-decyloxybenzoate and 4-*n*-decyloxyacetophenone and purified using the same procedure as for **3a**. Yield: 78 per cent.

Elemental analysis. Found (calculated for  $C_{35}H_{52}O_4$ ): C 78.32 per cent (78.36 per cent), H 9.77 per cent (9.70 per cent). IR  $\nu$   $cm^{-1}$ , NaCl: 3373 (OH), 1606 (C=O), 1513 (C=C).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.89 (t, 6 H,  $CH_3$ ), 1.28–1.39 (m, 28 H,  $-[CH_2]_{7-}$ ), 1.82 (m, 4 H,  $-CH_2-[CH_2]_{7-}$ ), 4.03 (t, 4 H,  $-OCH_2$ ), 6.73 (s, 1 H,  $-CH=$ enol), 6.96 (d, 4 H, aromatic- $H_{3,5}$ ), 7.95 (d, 4 H, aromatic- $H_{2,6}$ ), 17.16 (s, 1 H,  $-OH$  enol).

### 3.2.3. 1,3-bis(3,4-di-*n*-decyloxyphenyl)propane-1,3-dione (3c)

The compound was synthesized from methyl 3,4-di-*n*-decyloxybenzoate and 3,4-di-*n*-decyloxyacetophenone using the same procedure as for **3a**. The mixture was refluxed for 12 h. The crude precipitate was recrystallized from ethanol. Yield 63 per cent.

Elemental analysis. Found (calculated for  $C_{55}H_{92}O_6$ ): C 77.62 per cent (77.83 per cent), H 11.03 per cent (10.85 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3379 (OH), 1595 (C=O), 1514 (C=C).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.84 (m, 12 H,  $CH_3$ ), 1.23–1.45 (m, 56 H,  $-[CH_2]_{7-}$ ), 1.81 (m, 8 H,  $-CH_2-[CH_2]_{7-}$ ), 4.03 (m, 8 H,  $-OCH_2$ ), 6.67 (s, 1 H,  $-CH=$ enol), 6.87 (t, 2 H, aromatic- $H_5$ ), 7.51 (m, 4 H, aromatic- $H_{2,6}$ ), 17.14 (s, 1 H,  $-OH$  enol).

### 3.2.4. 1,3-bis(3,5-di-*n*-decyloxyphenyl)propane-1,3-dione (3d)

The compound was synthesized from methyl 3,5-di-*n*-decyloxybenzoate and 3,5-di-*n*-decyloxyacetophenone using the same procedure as for **3a**. It was purified by column chromatography in hexane/ether (13/1), Yield: 55 per cent.

Elemental analysis. Found (calculated for  $C_{55}H_{92}O_6$ ): C 77.91 per cent (77.83 per cent), H 10.93 per cent (10.85 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3384 (OH), 1590 (C=O), 1505 (C=C).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.88 (t, 12 H,  $CH_3$ ), 1.27–1.50 (m, 56 H,  $-[CH_2]_{7-}$ ), 1.80 (m, 8 H,  $-CH_2-[CH_2]_{7-}$ ), 4.00 (t, 8 H,  $-OCH_2$ ), 6.63 (t, 2 H, aromatic- $H_4$ ), 6.74 (s, 1 H,  $-CH=$ enol), 7.08 (d, 4 H, aromatic- $H_{2,6}$ ), 16.86 (s, 1 H,  $-OH$  enol).

## 3.3. Synthesis of the pyrazoles

### 3.3.1. 3,5-di(4-*n*-octyloxyphenyl)pyrazole (4a)

1.3 mmol of 1,3-di(4-*n*-octyloxyphenyl)propane-1,3-dione (**3a**) and 1 ml of hydrazine hydrate (80 per cent w/w) was refluxed in ethanol (25 ml) for 2 h and then stirred overnight at room temperature. The precipitated product was filtered with suction and purified by recrystallization from ethanol. Yield: 86 per cent.

Elemental analysis. Found (calculated for  $C_{31}H_{44}O_2N_2$ ): C 77.08 per cent (77.15 per cent), N 5.79 per cent (5.88 per cent), H 9.70 per cent (9.24 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3216 (NH), 1618, 1507 (pyrazole).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.88 (t, 6 H,  $CH_3$ ), 1.23–1.49 (m, 20 H,  $-[CH_2]_{5-}$ ), 1.80 m, 4 H,  $-CH_2-[CH_2]_{5-}$ , 3.96 (t, 4 H,  $-OCH_2$ ), 6.66 (s, 1 H,  $-CH=$ ), 6.90 (d, 4 H, aromatic- $H_{3,5}$ ), 7.62 (d, 4 H, aromatic- $H_{2,6}$ ).

### 3.3.2. 3,5-di(4-*n*-decyloxyphenyl)pyrazole (**4b**)

The compound was synthesized from 1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dione (**3b**) using the same procedure as for **4a**. The precipitated product was recrystallized from ethanol. Yield: 90 per cent.

Elemental analysis. Found (calculated for  $C_{35}H_{52}O_2N_2$ ): C 78.68 per cent (78.95 per cent), N 5.32 per cent (5.26 per cent), H 9.90 per cent (9.77 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3429 (NH), 1614, 1504 (pyrazole).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.89 (t, 6 H,  $CH_3$ ), 1.28–1.43 (m, 28 H,  $-[CH_2]_{7-}$ ), 1.81 (m, 4 H,  $-CH_2-[CH_2]_{7-}$ ), 4.00 (t, 4 H,  $-OCH_2$ ), 6.69 (s, 1 H,  $-CH=$ ), 6.96 (d, 4 H, aromatic- $H_{3,5}$ ), 7.63 (d, 4 H, aromatic- $H_{2,6}$ ).

### 3.3.3. 3,5-bis(3,4-di-*n*-decyloxyphenyl)pyrazole (**4c**)

The compound was synthesized from 1,3-bis(3,4-di-*n*-decyloxyphenyl)propane-1,3-dione (**3c**) using the same procedure as for **4a**. The precipitated product was recrystallized from acetone. Yield: 85 per cent.

Elemental analysis. Found (calculated for  $C_{55}H_{92}O_4N_2$ ): C 78.36 per cent (78.20 per cent), N 3.28 per cent (3.32 per cent), H 11.11 per cent (10.90 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3153 (NH), 1612, 1510 (pyrazole).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.87 (m, 12 H,  $CH_3$ ), 1.25–1.51 (m, 56 H,  $-[CH_2]_{7-}$ ), 1.84 (m, 8 H,  $-CH_2-[CH_2]_{7-}$ ), 4.05 (t, 4 H,  $-OCH_2$ ), 4.14 (t, 4 H,  $-OCH_2$ ), 6.80 (s, 1 H,  $-CH=$ ), 6.94 (t, 2 H, aromatic- $H_5$ ), 7.58 (d, 2 H, aromatic- $H_6$ ), 7.66 (s, 2 H, aromatic- $H_2$ ).

### 3.3.4. 3,5-bis(3,5-di-*n*-decyloxyphenyl)pyrazole (**4d**)

The compound was synthesized from 1,3-bis(3,5-di-*n*-decyloxyphenyl)propane-1,3-dione (**3d**) and purified using the same procedure as for **4a**. Yield: 82 per cent.

Elemental analysis. Found (calculated for  $C_{55}H_{92}O_4N_2$ ): C 78.29 per cent (78.20 per cent), N 3.34 per cent (3.32 per cent), H 10.81 per cent (10.90 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 3180 (NH), 1609, 1570 (pyrazole).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.87 (t, 12 H,  $CH_3$ ), 1.26–1.43 (m, 56 H,  $-[CH_2]_{7-}$ ), 1.76 (m, 8 H,  $-CH_2-[CH_2]_{7-}$ ), 3.93 (t, 8 H,  $-OCH_2$ ), 6.42 (t, 2 H, aromatic- $H_4$ ), 6.75 (s, 1 H,  $-CH=$ ), 6.82 (d, 4 H, aromatic- $H_{2,6}$ ).

## 3.4. Synthesis of the isoxazoles

### 3.4.1. 3,5-di(4-*n*-octyloxyphenyl)isoxazole (**5a**)

A mixture of 1 mmol of 1,3-di(4-*n*-octyloxyphenyl)propane-1,3-dione, 1 mmol of hydroxylamine hydrochloride and 1 mmol of triethylamine in 20 ml of ethanol was refluxed for 16 h and stirred overnight at room temperature. The precipitated product was collected by filtration and recrystallized from ethanol. Yield: 91 per cent.

Elemental analysis. Found (calculated for  $C_{31}H_{43}O_3N$ ): C 77.83 per cent (77.98 per cent), N 3.01 per cent (2.93 per cent), H 9.57 per cent (9.01 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 1602, 1509 (isoxazole).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.89 (m, 6 H,  $CH_3$ ), 1.20–1.46 (m, 20 H,  $-[CH_2]_{5-}$ ), 1.81 (m, 4 H,  $-CH_2-[CH_2]_{5-}$ ), 4.00 (m, 4 H,  $-OCH_2$ ), 6.64 (s, 1 H,  $-CH=$ ), 6.97 (d, 4 H, aromatic- $H_{3,5}$  and  $H_{3',5'}$ ), 7.76 (dd, 4 H, aromatic- $H_{2,6}$  and  $H_{2',6'}$ ).

### 3.4.2. 3,5-di(4-*n*-decyloxyphenyl)isoxazole (**5b**)

The compound was synthesized from 1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dione (**3b**) and purified using the same procedure as for **5a**. Yield: 90 per cent.

Elemental analysis. Found (calculated for  $C_{35}H_{51}O_3N$ ): C 78.94 per cent (78.80 per cent), N 2.59 per cent (2.63 per cent), H 9.74 per cent (9.57 per cent). IR,  $\nu$   $cm^{-1}$ , NaCl: 1617, 1508 (isoxazole).  $^1H$  NMR,  $\delta$  ppm,  $CDCl_3$ : 0.89 (m, 6 H,  $CH_3$ ), 1.28–1.50 (m, 28 H,

$-\text{[CH}_2\text{]}_{7-}$ ), 1.81 (m, 4 H,  $-\text{CH}_2-\text{[CH}_2\text{]}_{7-}$ ), 4.01 (m, 4 H,  $-\text{OCH}_2$ ), 6.65 (s, 1 H,  $-\text{CH}=\text{)$ , 6.98 (d, 4 H, aromatic- $\text{H}_{3,5}$  and  $\text{H}_{3',5'}$ ), 7.77 (dd, 4 H, aromatic- $\text{H}_{2,6}$  and  $\text{H}_{2',6'}$ ).

### 3.4.3. 3,5-bis(3,4-di-*n*-decyloxyphenyl)isoxazole (**5c**)

The compound was synthesized from 1,3-bis(3,4-di-*n*-decyloxyphenyl)propane-1,3-dione (**3c**) using the same procedure as for **5a**. It was recrystallized from acetone. Yield: 78 per cent.

Elemental analysis. Found (calculated for  $\text{C}_{55}\text{H}_{91}\text{O}_5\text{N}$ ): C 77.98 per cent (78.11 per cent), N 1.71 per cent (1.66 per cent), H 10.88 per cent (10.77 per cent). IR,  $\nu\text{ cm}^{-1}$ , NaCl: 1606, 1509 (isoxazole).  $^1\text{H NMR}$ ,  $\delta$  ppm,  $\text{CDCl}_3$ : 0.87 (m, 12 H,  $\text{CH}_3$ ), 1.27–1.48 (m, 56 H,  $-\text{[CH}_2\text{]}_{7-}$ ), 1.83 (m, 8 H,  $-\text{CH}_2-\text{[CH}_2\text{]}_{7-}$ ), 4.06 (m, 8 H,  $-\text{OCH}_2$ ), 6.64 (s, 1 H,  $-\text{CH}=\text{)$ , 6.93 (t, 2 H, aromatic- $\text{H}_5$  and  $\text{H}_{5'}$ ), 7.39 (m, 4 H, aromatic- $\text{H}_{2,6}$  and  $\text{H}_{2',6'}$ ).

### 3.4.4. 3,5-bis(3,5-di-*n*-decyloxyphenyl)isoxazole (**5d**)

The compound was synthesized from 1,3-bis(3,5-di-*n*-decyloxyphenyl)propane-1,3-dione (**3d**) using the same procedure as for **5a**. It was purified by column chromatography in hexane/ether (19/1). Yield: 77 per cent.

Elemental analysis. Found (calculated for  $\text{C}_{55}\text{H}_{91}\text{O}_5\text{N}$ ): C 78.19 per cent (78.11 per cent), N 1.63 per cent (1.66 per cent), H 10.89 per cent (10.77 per cent). IR,  $\nu\text{ cm}^{-1}$ , NaCl: 1602, 1578 (isoxazole).  $^1\text{H NMR}$ ,  $\delta$  ppm,  $\text{CDCl}_3$ : 0.87 (m, 12 H,  $\text{CH}_3$ ), 1.27–1.45 (m, 56 H,  $-\text{[CH}_2\text{]}_{7-}$ ), 1.79 (m, 8 H,  $-\text{CH}_2-\text{[CH}_2\text{]}_{7-}$ ), 3.99 (m, 8 H,  $-\text{OCH}_2$ ), 6.53 (m, 2 H, aromatic- $\text{H}_4$  and  $\text{H}_4'$ ), 6.74 (s, 1 H,  $-\text{CH}=\text{)$ , 6.96 (dd, 4 H, aromatic- $\text{H}_{2,6}$  and  $\text{H}_{2',6'}$ ).

## 3.5. Synthesis of the thallium (I) complex

### 3.5.1. [1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dionate]thallium (I) (**6b**)

1 mmol of thallium(I) ethoxide was added dropwise to a stirred solution of 1 mmol of 1,3-di(4-*n*-decyloxyphenyl)propane-1,3-dione (**3b**) in an inert solvent such as toluene or petroleum ether. Hexane was added to precipitate the complex. The mixture was stirred for 3 h. The precipitated product was collected by filtration with suction and purified by recrystallization from hexane. Yield: 86 per cent.

Elemental analysis. Found (calculated for  $\text{C}_{35}\text{H}_{51}\text{O}_4\text{Tl}$ ): C 56.82 per cent (56.80 per cent), H 6.87 per cent (6.90 per cent).

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