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β-Diketone, pyrazole and isoxazole derivatives with polar groups: Liquid crystalline and non-linear optical properties

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The liquid crystalline behaviour of 1-(4-*n*-decyloxyphenyl)-3-(4-X-phenyl)propan-1,3-diones and their pyrazole and isoxazole derivatives has been studied by optical microscopy, DSC and X-ray techniques. The 4-substituents (X) were chosen to include a range of different polar and non-polar substituents: H, OCH_3, Cl, Br and CN. A monotropic S_A phase is observed for the β-diketone derivative in which X = CN and this is the first example of this phase found in a 1,3-diphenylpropan-1,3-dione derivative. The majority of the pyrazole and isoxazole compounds show S_A phases. As regards the cyano-substituted compounds, X-ray diffraction studies on the mesophase show that the layer spacing is consistent with a partial bilayer S_A mesophase. The first hyperpolarizabilities of the cyano-derivatives due to their push–pull structure have been measured by the EFISH method. Values for these compounds were found to be comparable to those for other conjugated CH_3O–π–CN systems.

1. Introduction

β-Diketones have proven to be very efficient as starting materials for various kinds of mesogenic compounds. In particular, aromatic β-diketonate copper(II) complexes bearing two long alkoxy groups in the 3- and 4-positions of each benzene ring have been shown to exhibit columnar mesomorphism [1]. More recently, similar behaviour has been found for β-diketonate copper(II), palladium(II) and oxovanadiuim(IV) complexes with ten or twelve alkoxy chains [2]. The analogous complexes having only one alkoxy group in the 4-position of each aromatic ring have been reported to exhibit layered phases (assigned as discotic lamellar) [3, 4]. Columnar mesomorphism has also been described in half-disc shaped complexes of thallium(I) in which four or five alkoxy groups are present in the β-diketonate ligand. In these cases the columns are generated by stacking of disc-shaped dimers [5].

Purely organic mesogenic β-diketone derivatives have also been reported. Calamitic mesomorphism has been described in a number of pyrazoles and isoxazoles derived from 4-alkoxy substituted aromatic β-diketones [6, 7]. These compounds exhibit classical nematic and smectic A and C mesophases despite the fact that the molecules have a bent banana-shape rather than a rod-like shape, due to the substitution in the 3- and 5-positions of the central five-membered heterocycle.

In this paper, we have extended the study of the liquid crystal behaviour of these systems to include non-symmetrical aromatic β-diketones, specifically 1-(4-*n*-decyloxyphenyl)-3-(4-X-phenyl)propan-1,3-diones and their pyrazole and isoxazole derivatives. The substituent (X) was chosen to include different polar and non-polar groups (H, OCH_3, Cl, Br, and CN), with the aim of discussing the influence of these groups on the mesogenic behaviour. The liquid crystalline properties were studied by optical microscopy and differential scanning calorimetry (DSC), and the synthetic route employed is given in figure 1.

In addition to the structure/mesogenic property study, the presence of strongly polar, highly polarizable groups in some of these compounds makes them potentially interesting for their ability to exhibit second order non-linear optical properties. In particular, the compounds which contain the cyano-group have an electron-acceptor substituent and an electron-donor substituent at the ends of a conjugated system, which leads to an

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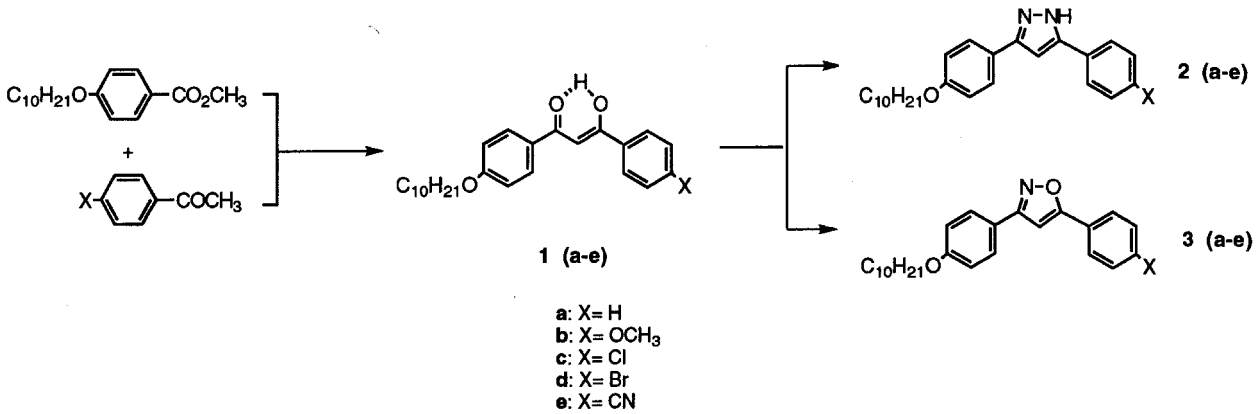


Figure 1. Synthetic route to the β-diketone, pyrazole and isoxazole derivatives.

intramolecular charge transfer effect of π-electrons. Therefore, the cyano-derivatives (β-diketone, pyrazole and isoxazole) were tested for non-linear optical properties; the first hyperpolarizability coefficient β of the three cyano-derivatives in solution was measured by the electric field induced second harmonic (EFISH) technique [8].

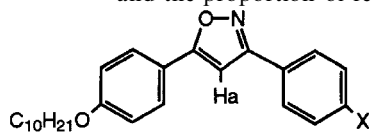
2. Characterization of the compounds

All compounds have been characterized by ^{1}H NMR and IR spectroscopy. The results are summarized in the Experimental section (§5). The ^{1}H NMR spectra show that the β-diketones exist in the enol form. A singlet is observed between 6·7 and 6·8 ppm, depending on the β-diketone, which corresponds to the central CH proton. Another singlet is observed at *ca.* 17 ppm and corresponds to the OH proton.

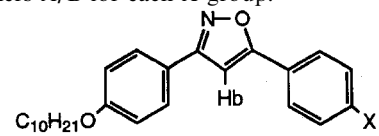
Unsymmetrical β-diketones and pyrazoles would be expected to give rise to a mixture of two tautomers in equilibrium in solution (the two enol forms), but the ^{1}H NMR data provide no evidence of the existence of different tautomers. This indicates that the interchange of the proton is too fast to be detected by this spectroscopic technique.

The isoxazole derivatives were obtained as a mixture of two regioisomers arising from the attack of hydroxylamine on one or other of the enol tautomers of the precursor β-diketone. The presence of both isomers is confirmed by observation of the ^{1}H NMR signal corresponding to the CH proton of the isoxazole ring (see table 1). Two singlets are found for all derivatives. The relative proportion of regioisomers A/B is 50/50 for the methoxy derivative (compound **3b**), whereas for the others, it is around 70/30. The main regioisomer is A, in which the nitrogen atom of the heterocycle is nearest to the aromatic ring bearing the substituent X. The presence of two isomers also complicates the signals due to the benzene protons. The effect is greatest on the protons *ortho* to the heterocyclic ring, but the assignment is further complicated by partial overlap of the aromatic signals.

Table 1. ^{1}H NMR chemical shifts of the proton of the isoxazole ring and the proportion of regioisomers A/B for each X group.



A



B

Compound (X)	δHa (ppm)	δHb (ppm)	A/B
3a (H)	6·68	6·76	78/22
3b (OCH_3)	6·63	6·63	50/50
3c (Cl)	6·65	6·75	65/35
3d (Br)	6·65	6·76	73/27
3e (CN)	6·70	6·88	69/31

3. Liquid crystalline properties

The results of the optical and calorimetric studies are given in table 2 for the β-diketone, pyrazole and isoxazole derivatives.

3.1. *Study of the* β-*diketones*

The β-diketones **1a–d** are not mesomorphic, which was expected on the basis of the results found for similar β-diketones previously studied [6]. This can be accounted for by considering the bent geometry of the propan-1,3-dione system, deduced from diffraction data of other β-diketones taken from the literature [9]. The pronounced non-bending linearity of the molecular core precludes mesomorphism.

However, compound **1e** shows a monotropic mesophase, identified as smectic A by its focal-conic texture. In the DSC cooling scan, the low value of the transition enthalpy (1·9 KJ mol^{-1}) for the peak at 66·0°C is in good agreement with that expected for an isotropic liquid–smectic A mesophase transition. Although smectic A phases have been found for β-diketones bearing biphenylyl and cyano groups [10], this is the first time that a smectic A phase has been observed in a 1,3-diphenylpropan-1,3-dione derivative, and the fact that this phase is observed could be attributed to the strong dipole moment of the cyano group which is known to favour an antiparallel arrangement of the molecular dipoles [11], see figure 2. In this way, the resulting increase in the clearing point, even though the molecules are not linear, makes the appearance of the mesophase possible before crystallization occurs on cooling the isotropic liquid.

3.2. *Study of the pyrazoles and isoxazoles*

All the pyrazoles studied, with the exception of compound **2a**, exhibit liquid crystal behaviour, in each case showing an enantiotropic smectic A mesophase identified by its typical homeotropic and focal-conic textures

Table 2. Optical, thermal and thermodynamic data for the β-diketone (**1**), pyrazole (**2**) and isoxazole (**3**) derivatives.

Compound	X	Transition	T/°C	ΔH/KJ mol^{-1}
1a	H	Cr–I	49·1	34·5
1b	CH_3O	Cr–I	69·6	44·5
1c	Cl	Cr–I	81·5	46·0
1d	Br	Cr–I	89·4	42·3
1e	CN	Cr_1–Cr_2	46·7	6·2
		Cr_2–I	82·6	32·1
		I–S_A	66·0	1·9
2a	H	Cr–I	90·5	30·6
2b	CH_3O	Cr–S_A	106·7	39·0
		S_A–I	180·9	3·7
2c	Cl	Cr_1–Cr_2[a]	99·0	32·6
		Cr_2–S_A	154·1	9·8
		S_A–I	221·7	8·2
2d	Br	Cr_1–Cr_2[a]	112·7	32·1
		Cr_2–S_A	163·3	10·5
		S_A–I	224·0	8·2
2e	CN	Cr–S_A	159·9	35·5
		S_A–I	186·0	3·1
3a	H	Cr–I	98·0	44·9
		I–S_A	93·0	43·3
		S_A–Cr	90·7	—
3b	CH_3O	Cr–N	101·6	43·7
		N–I	152·5	0·6
3c	Cl	Cr_1–Cr_2	94·5	37·9
		Cr_2–S_A	97·4	6·3
		S_A–I	175·2	—
3d	Br	Cr_1–Cr_2[a]	77·0	28·7
		Cr_2–S_A	112·3	12·4
		S_A–I	186·7	7·9
3e	CN	Cr_1–Cr_2[a]	64·8	0·5
		Cr_2–Cr_3[a]	77·7	7·8
		Cr_3–S_A	91·8	30·8
		S_A–I	183·6	3·6

[a] Only seen in the first heating.

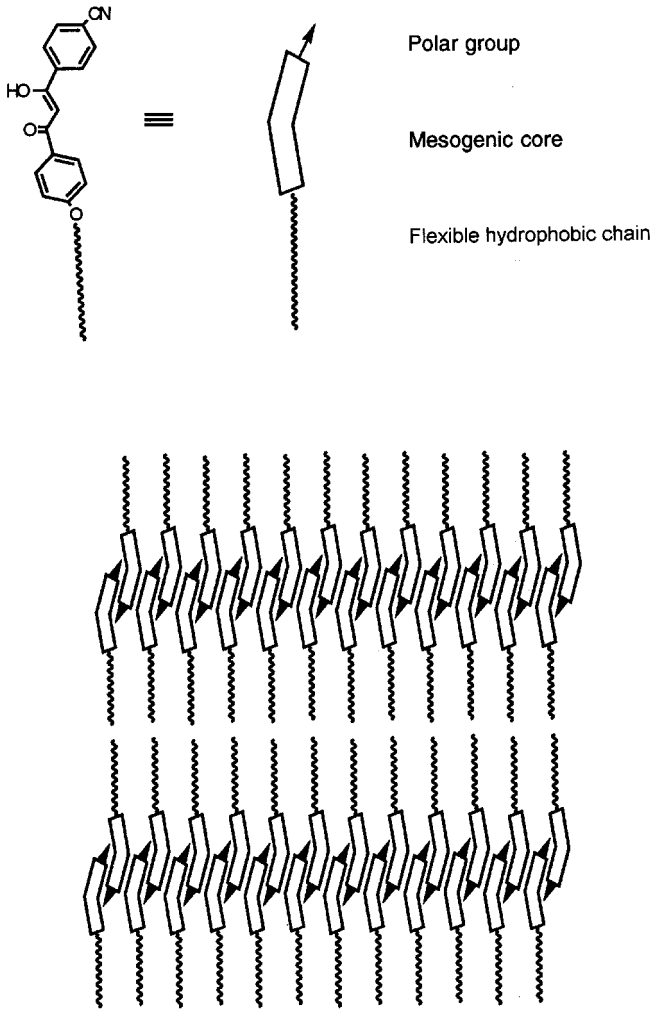


Figure 2. Schematic representation of the proposed partial bilayer smectic A phase of compound **1e**.

(compounds **2b–e**). Similarly, all the isoxazoles studied exhibit mesomorphism: nematic for **3b** (assigned by its threaded texture), monotropic smectic A for **3a**, and enantiotropic smectic A for **3c–e** (assigned by their homeotropic and focal-conic textures).

It seems likely that, in comparison with the β-diketones, the increased mesogenic character of the pyrazole and isoxazole derivatives is due to their conjugated character and their high dipole moments, both of which favour mesophase formation and, in particular, smectic phases. In addition to this, and in contrast to the β-diketones, the geometry of the pyrazoles and isoxazoles deviates only very slightly from linearity, as deduced from diffraction data taken from the literature [12] and from AM1 [13] and CNDO/2 calculations.

3.3. *Comparative study*

If we compare the clearing points of the pyrazole and isoxazole derivatives, we observe that they are higher for the pyrazoles than the isoxazoles (see table 2). This could be due to the existence of higher structural order in the pyrazoles because they are more symmetrical and they have the ability to form intermolecular hydrogen bonds. In fact, infrared spectroscopic studies previously carried out in our laboratory [6] show the occurrence of hydrogen bonding in the mesophase of similar pyrazoles ($X = OC_{10}H_{21}$). Indeed, the stretching vibration of the nitrogen–hydrogen bond in both the mesophase and in the isotropic phase gives two bands of a similar intensity which correspond to the free ($3419\,cm^{-1}$) and associated ($3259\,cm^{-1}$) species. The fact that pyrazole **2b** shows a smectic A mesophase, whereas the isoxazole **3b** with the same substituent shows a nematic mesophase (with a lower degree of organization) is also in good agreement with the existence of a higher structural order in the pyrazoles.

With regard to the melting points, the pyrazole derivatives also involve higher temperatures than the isoxazole derivatives.

In both series of compounds, the presence of a polar group ($X \neq H$) noticeably favours mesomorphism and increases the clearing points. Thus, the unsubstituted pyrazole **2a** ($X = H$) does not show any mesomorphic behaviour, whereas the other pyrazole derivatives do. In the isoxazole series, the mesophase of the non-substituted isoxazole **3a** ($X = H$) is only monotropic, whereas the other derivatives have enantiotropic phases. Within the series of polar groups, Cl, Br and CN give rise to the highest clearing points.

3.4. *X-ray study*

The mesophases of the compounds described in this paper were studied by X-ray diffraction. In all cases, the X-ray photographs confirmed the type of mesophase assigned on the basis of the microscopic textures. Thus, the diffraction patterns recorded in the nematic phase display only two diffuse haloes at small and large angles, corresponding to the short range correlations parallel and perpendicular to the director, respectively. The smectic A mesophase gives a sharp ring at small angles, characteristic of the interlayer periodicity, and a diffuse band at large angles, characteristic of the absence of intralayer long range order. For the bromo-substituted compounds, the presence of the heavy atom makes the observation of the second order reflection at small angles possible, thus confirming the lamellar order. The layer periodicities measured for the smectic mesophases are gathered in table 3.

From these data it can be concluded that, in general, the layer spacing d varies very little on changing the substituent, with the exception of the cyano derivatives (compounds **2e** and **3e**) which have a significantly larger value. Moreover, the experimental value for compounds

Table 3. X-ray diffraction data for the smectic A mesophase of the pyrazoles (compounds **2b–e**) and isoxazoles (compounds **3c–e**). d = measured layer spacing ($\pm 0{\cdot}5$ Å); L = molecular length estimated from Dreiding stereomodels (± 1 Å).

Compound	X	T/°C	d/Å	L/Å
2b	CH_3O	143	29·5	30
2c	Cl	180	28·9	28
2d	Br	180	29·5	28
2e	CN	172	36·2	29
3c	Cl	145	29·3	28
3d	Br	145	29·9	28
3e	CN	145	35·7	29

2b–d and **3c–d** ($d = 29$–30 Å) compares well with the molecular length estimated from Dreiding stereomodels ($L = 28$–30 Å), whereas the experimental value for the cyano compounds ($d = 36$ Å) is greater than the estimated molecular length ($L = 29$ Å). This is consistent with a partial bilayer smectic A mesophase, typically found in many mesogens incorporating strongly polar terminal groups, and it is due to the antiparallel association between dipoles. Unfortunately we were unable to study the monotropic mesophase of the cyano-substituted β-diketone (compound **1e**) due to rapid crystallisation on cooling. However, the same kind of dipole association is the most plausible explanation of the fact that this compound is the only β-diketone to exhibit mesomorphism (see figure 2).

4. Non-linear optical properties

Compounds **1e**, **2e** and **3e** were tested for non-linear optical behaviour because of their push–pull structure. The first hyperpolarizability β was measured using solutions (1,4-dioxane) at 1·38 μm and the EFISH method [8(*c*), 14].

The maximum of the absorption band λ_{max}, as well as the $\mu\beta$, $\mu\beta_0$, β, β_0, and μ values are reported in table 4. The static values $\mu\beta_0$ and β_0 (extrapolated to infinite wavelengths) have been calculated according to the two-level model [8(*c*)]. The dipole moments were obtained independently from dielectric constant measurements using the Guggenheim method.

The measurements on compound **3e** were performed on the mixture of the two regioisomers because all efforts to separate them were unsuccessful. The two structures have been optimized by means of semi-empirical calculations (AM1, MOPAC package), and we found that the direction of the dipole moment is essentially the same in both isomers (the moduli are also very similar). This indicates that a change in the position of the heteroatoms within the isoxazole ring has very little effect on the direction of μ, and the most important contribution is due to the cyano-substituent. From these calculations we deduced that the measured first hyperpolarizability along the dipole moment (β_{EFISH}) for **3e** would be an average of the β_{EFISH} value of each regioisomer.

The absorbance spectra of these compounds show that they are very transparent, especially the heterocyclic derivatives (compounds **2e** and **3e**) which have their absorption maxima below 350 nm (see figure 3).

Compound **1e** shows higher β values than **2e** and **3e** which is consistent with a known relationship between β and the long wavelength absorption maximum [15]. To the best of our knowledge, β_{EFISH} values for β-diketones have not been reported in the literature and this is the first time that the properties of a β-diketone have been measured by the EFISH method. The lower β values obtained for pyrazole and isoxazole derivatives could be due to the higher aromatic character of these moieties as compared to the diketone, thus stabilizing the molecules in their ground state and limiting the intramolecular charge transfer which would break this aromaticity.

The compounds reported here can be compared with other RO–π–CN systems. The comparisons are, however, only qualitative due to the difference in the experimental procedure in each case. It can be concluded that a two-atom conjugated bridge (such as in the stilbene compound A or the Schiff's bases B and C in table 5) is more effective than a three-atom bridge as found in the β-diketone, pyrazole or isoxazole systems. This indicates that the charge transfer is less efficient, possibly because the two phenyl rings can only interact weakly via the three-atom systems.

The measured β values are more similar to that of the biphenyl derivative D, where the existence or torsional angles between the phenyl rings makes the charge transfer between the methoxy and cyano groups difficult, and the polarization is confined to the region near these groups and not distributed over the whole molecule.

Table 4. Absorbance maxima λ_{max}/nm; EFISH data: $\mu\beta/(10^{48}$ esu), $\beta/(10^{30}$ esu) and dipole moments μ/D of the cyano-derivatives.

Compound	λ_{max}	$\mu\beta_{1\cdot34}$	$\mu\beta_0$	μ	$\beta_{1\cdot34}$	β_0
1e	363	74 ± 7	$49{\cdot}8 \pm 4{\cdot}7$	$6{\cdot}5 \pm 1$	$11{\cdot}8 \pm 3$	$7{\cdot}9 \pm 2$
2e	276	42 ± 5	$34{\cdot}3 \pm 4{\cdot}1$	$7{\cdot}5 \pm 1$	$5{\cdot}8 \pm 1{\cdot}5$	$4{\cdot}7 \pm 1{\cdot}2$
3e	274	33 ± 3	$27{\cdot}0 \pm 2{\cdot}5$	6 ± 1	$5{\cdot}7 \pm 1{\cdot}5$	$4{\cdot}6 \pm 1{\cdot}2$

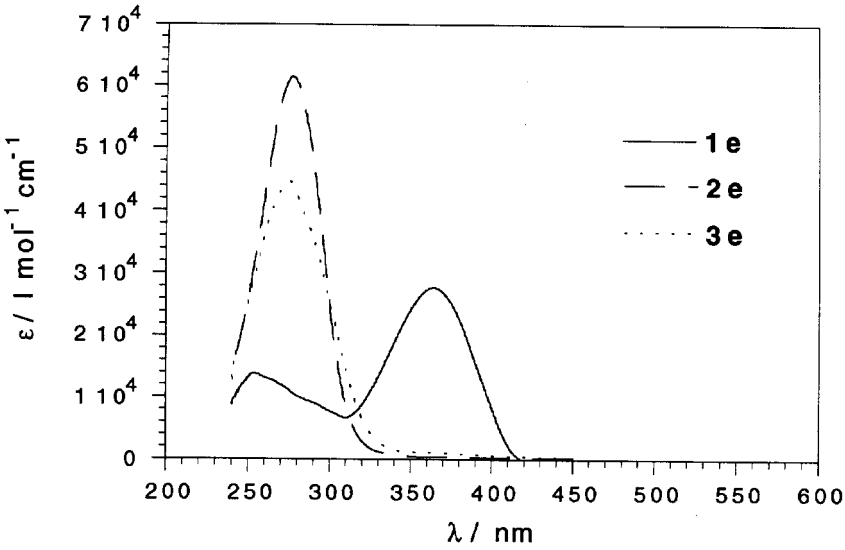
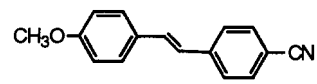
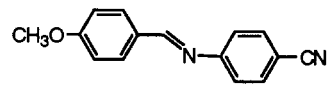
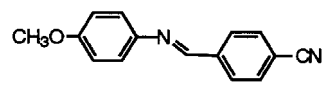
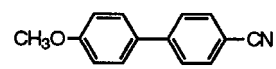
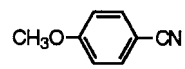


Figure 3. Normalized UV-VIS spectra of the cyano-derivatives in 1,4-dioxane solution.

Table 5. EFISH data for similar systems (RO–π–CN).

	Compound	EFISH data	Ref.
A		$\beta = 19$ (DMSO, $\lambda = 1{\cdot}9\,\mu m$)	[15]
B		$\beta = 16 \pm 8$ (acetone, $\lambda = 1{\cdot}06\,\mu m$)	[16]
C		$\beta = 23 \pm 10$ (acetone, $\lambda = 1{\cdot}06\,\mu m$)	[16]
D		$\beta = 6{\cdot}3$ (dioxane, $\lambda = 1{\cdot}9\,\mu m$)	[15]
E		$\beta = 1{\cdot}9$ (dioxane, $\lambda = 1{\cdot}9\,\mu m$)	[15]

5. Experimental

5.1. *General considerations*

The compounds have been characterized by ^{1}H NMR and IR spectroscopy, and mass spectrometry. ^{1}H NMR spectra were recorded using a Varian XL-200 spectrometer. IR spectra were obtained using a Perkin-Elmer 1600 (FTIR series) spectrometer. Mass spectra were obtained using a VG Autospec (FAB^+, NBA matrix) spectrometer. The optical textures of the mesophases were studied with an Olympus polarizing microscope equipped with a Linkam THMS 600 hot stage and a central processor. The transition temperatures and enthalpies of transition were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 instrument operated at a scanning rate of $10°\,min^{-1}$ on heating. The apparatus was calibrated with indium (156·6°C, $28{\cdot}4\,J\,g^{-1}$) and tin (232·1°C, $60{\cdot}46\,J\,g^{-1}$) as standards. X-ray diffraction patterns were obtained using a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu Kα beam. The samples were held in Lindemann glass capillaries (1 mm diameter) and heated with a variable-temperature attachment. The

diffraction patterns were collected on flat photographic film. The absorption spectra were obtained using a Kontron Uvikon 941 Plus Spectrometer. The EFISH measurements were made using an NLO spectrometer from SOPRA.

5.2. *Synthesis of the* β*-diketones*

5.2.1. *1-(4-*n*-Decyloxyphenyl)-3-phenylpropan-1,3-dione* (**1a**)

Sodium hydride (97%, 0.6 g, 24·1 mmol) was added to a solution of methyl 4-*n*-decyloxybenzoate (12 mmol) and acetophenone (12 mmol) in dry 1,2-dimethoxyethane. The mixture was heated under reflux for two hours and stirred overnight at room temperature. A small amount of water was added carefully to the reaction mixture, followed by acidification with dilute hydrochloric acid. The product was extracted into ether, washed with saturated aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulphate, filtered and evaporated to dryness. The crude product was dissolved in hot hexane and the solution filtered when it was cold. The solvent was removed and the residue recrystallized from ethanol. Yield: 32%. IR, ν cm^{-1}, NaCl: 1605 (C=O), 1587 (C=C), ^{1}H NMR, δ ppm, $CDCl_3$: 0·89 (t, J = 6·6 Hz, 3H, $-CH_3$), 1·28–1·50 (m, 14H, $-(CH_2)7-CH_3$), 1·77–1·84 (m, 2H, $-O-CH_2-CH_2-$), 4·04 (t, J = 6·6 Hz, 2H, $-OCH_2-$), 6·80 (s, 1H, –CH=enol), 6·97 (d, J = 8·7 Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·46–7·55 (m, 3H, unsub. phenyl $H_{3,5}$ and H_4), 7·98 (d, J = 8·7 Hz, 4H, both aromatic rings $H_{2,6}$), 17·02 (s, 1H, OH enol). MS: *m/z* (%): 381 (100, $(M+1]^+$), 261 (33, $C_{17}H_{25}O_2^+$).

5.2.2. *1-(4-*n*-Decyloxyphenyl)-3-(4-methoxyphenyl)-propan-1,3-dione* (**1b**)

This compound was synthesized from methyl 4-*n*-decyloxybenzoate and 4-methoxyacetophenone using the same procedure as for **1a**. It was purified by recrystallization from ethanol and then from hexane. Yield: 55%. IR, ν cm^{-1}, NaCl: 1605 (C=O), 1587 (C=C). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, J = 6·7 Hz, 3H, $-CH_3$), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·76–1·81 (m, 2H, $-O-CH_2-CH_2-$), 3·86 (s, 3H, $-OCH_3$), 4·00 (t, J = 6·4 Hz, 2H, $-OCH_2-$), 6·71 (s, 1H, –CH=enol), 6·93 (d, J = 8·6 Hz, 2H, decyloxyphenyl $H_{3,5}$), 6·95 (d, J = 8·6 Hz, 2H, methoxyphenyl $H_{3,5}$), 7·92 (d, J = 8·6 Hz, 2H, methoxyphenyl $H_{2,6}$), 7·93 (d, J = 8·6 Hz, 2H, decyloxyphenyl $H_{2,6}$), 17·13 (s, 1H, OH enol). MS: *m/z* (%): 411 (100, $[M+1]^+$), 261 (60, $C_{17}H_{25}O_2^+$).

5.2.3. *1-(4-Chlorophenyl)-3-(4-*n*-decyloxyphenyl)-propan-1,3-dione* (**1c**)

This compound was synthesized from methyl 4-*n*-decyloxybenzoate and 4-chloroacetophenone using the same procedure as for **1a**. It was recrystallized twice from ethanol. Yield: 62%. IR, ν cm^{-1}, NaCl: 1606 (C=O), 1584 (C=C). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, J = 6·7 Hz, 3H, $-CH_3$), 1·28–1·33 (m, 14H, $-(CH_2)_7-CH_3$), 1·76–1·79 (m, 2H, $-O-CH_2-CH_2-$), 4·01 (t, J = 6·4 Hz, 2H, $-OCH_2-$), 6·73 (s, 1H, –CH=enol), 6·94 (d, J = 9·0 Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·43 (d, J = 8·8 Hz, 2H, chlorophenyl $H_{3,5}$), 7·89 (d, J = 8·7 Hz, 2H, chlorophenyl $H_{2,6}$), 7·94 (d, J = 9·0 Hz, decyloxyphenyl $H_{2,6}$), 16·96 (s, 1H, OH enol). MS: *m/z* (%): 415 (100, $[M+1]^+$).

5.2.4. *1-(4-Bromophenyl)-3-(4-*n*-decyloxyphenyl)-propan-1,3-dione* (**1d**)

This compound was synthesized from methyl 4-*n*-decyloxybenzoate and 4-bromoacetophenone using the same procedure as for **1a**. It was recrystallized twice from ethanol. Yield: 54%. IR, ν cm^{-1}, NaCl: 1605 (C=O), 1587 (C=C). ^{1}H NMR, δ ppm, $CDCl_3$: 0·87 (t, J = 6·5 Hz, 3H, $-CH_3$), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·77–1·82 (m, 2H, $-O-CH_2-CH_2-$), 4·02 (t, J = 6·5 Hz, 2H, $-OCH_2-$), 6·73 (s, 1H, –CH=enol), 6·95 (d, J = 8·8 Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·60 (d, J = 8·2 Hz, 2H, bromophenyl $H_{3,5}$), 7·82 (d, J = 8·2 Hz, 2H, bromophenyl $H_{2,6}$), 7·94 (d, J = 8·8 Hz, 2H, decyloxyphenyl $H_{2,6}$), 16·94 (s, 1H, OH enol). MS: *m/z* (%): 459 (100, $[M+1]^+$).

5.2.5. *1-(4-Cyanophenyl)-3-(4-*n*-decyloxyphenyl)-propan-1,3-dione* (**1e**)

This compound was synthesized from methyl 4-*n*-decyloxybenzoate and 4-acetylbenzonitrile using the same procedure as for **1a**. The mixture was heated under reflux for 3 h. The product was purified by column chromatography using hexane/ethyl acetate (15:1) as eluent, followed by recrystallization from ethanol. Yield: 14%. IR, ν cm^{-1}, NaCl: 3568, 3493 (OH), 2228 (CN), 1603 (C=O), 1585 (C=C). ^{1}H NMR, δ ppm, $CDCl_3$: 0·86 (t, J = 6·6 Hz, 3H, $-CH_3$), 1·26–1·47 (m, 14H, $-(CH_2)_7-CH_3$), 1·77–1·82 (m, 2H, $-O-CH_2-CH_2-$), 4·02 (t, J = 6·6 Hz, 2H, $-OCH_2-$), 6·78 (s, 1H, –CH=enol), 6·95 (d, J = 9·0 Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·75 (d, J = 8·5 Hz, 2H, cyanophenyl $H_{3,5}$), 7·95 (d, J = 9·0 Hz, 2H, decyloxyphenyl $H_{2,6}$), 8·02 (d, J = 8·5 Hz, 2H, cyanophenyl $H_{2,6}$), 16·80 (s, 1H, OH enol). MS: *m/z* (%): 406 (100, $[M+1]^+$), 261 (74, $C_{17}H_{25}O_2^+$).

5.3. *Synthesis of the pyrazoles*

5.3.1. *3-(4-*n*-Decyloxyphenyl)-5-phenylpyrazole* (**2a**)

To a suspension of 1-(4-*n*-decyloxyphenyl)-3-phenylpropan-1,3-dione (**1a**) (2 mmol) in ethanol (30 ml) was added hydrazine hydrate (80%, 1·5 ml, 24·7 mmol). The mixture was heated under reflux for 2 h and then stirred overnight at room temperature. The solid was filtered off and recrystallized from ethanol. Yield: 68%. IR, ν cm^{-1}, NaCl: 3235 (NH), 1618, 1508 (pyrazole). ^{1}H

NMR, δ ppm, $CDCl_3$: 0·88 (t, $J = 6{\cdot}4$ Hz, 3H, $-CH_3$), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·75–1·80 (m, 2H, $-O-CH_2-CH_2-$), 3·94 (t, $J = 6{\cdot}4$ Hz, 2H, $-OCH_2-$), 6·71 (s, 1H, $-CH=$), 6·87 (d, $J = 8{\cdot}4$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·29–7·38 (m, 3H, unsub. phenyl $H_{3,5}$ and H_4), 7·59 (d, $J = 8{\cdot}4$ Hz, 2H, decyloxyphenyl $H_{2,6}$), 7·69 (d, $J = 7{\cdot}0$ Hz, 2H, unsub. phenyl $H_{2,6}$), 11·2 (broad s, 1H, NH). MS: *m/z* (%): 377 (100, $[M+1]^+$), 236 (54, $([M+1]-C_{10}H_{21})^+$).

5.3.2. *3-(4-*n*-Decyloxyphenyl)-5-(4-methoxyphenyl)-pyrazole* (**2b**)

This compound was synthesized from 1-(4-*n*-decyloxyphenyl)-3-(4-methoxyphenyl)propan-1,3-dione (**1b**) using the same procedure as described for **2a**. Yield: 88%. IR, $\nu\,cm^{-1}$, NaCl: 3244 (NH), 1616, 1506 (pyrazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}6$ Hz, 3H, CH_3), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·76–1·81 (m, 2H, $-O-CH_2-CH_2-$), 3·83 (s, 3H, $-OCH_3$), 3·97 (t, $J = 6{\cdot}6$ Hz, 2H, $-OCH_2-$), 6·67 (s, 1H, $-CH=$), 6·92 (d, $J = 8{\cdot}8$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 6·93 (d, $J = 8{\cdot}8$ Hz, 2H, methoxyphenyl $H_{3,5}$), 7·60–7·65 (m, 4H, both aromatic rings $H_{2,6}$), 10·4 (broad s, 1H, NH). MS: *m/z* (%): 407 (100, $[M+1]^+$), 266 (33, $([M+1]-C_{10}H_{21})^+$).

5.3.3. *3-(4-Chlorophenyl)-5-(4-*p*-n-decyloxyphenyl)-pyrazole* (**2c**)

This compound was synthesized from 1-(4-chlorophenyl)-3-(4-*n*-decyloxyphenyl)propan-1,3-dione (**1c**) using the same procedure as described for **2a**. Yield: 85%. IR, $\nu\,cm^{-1}$, NaCl: 3244 (NH), 1615, 1493 (pyrazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}2$ Hz, 3H, $-CH_3$), 1·23–1·56 (m, 14H, $-(CH_2)_7-CH_3$), 1·78–1·79 (m, 2H, $-O-CH_2-CH_2-$), 3·99 (t, $J = 6{\cdot}4$ Hz, 2H, $-OCH_2-$), 6·68 (s, 1H, $-CH=$), 6·88 (d, $J = 8{\cdot}6$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·33 (d, $J = 8{\cdot}6$ Hz, 2H, chlorophenyl $H_{3,5}$), 7·53 (d, $J = 8{\cdot}6$ Hz, 2H, decyloxyphenyl $H_{2,6}$), 7·65 (d, $J = 8{\cdot}6$ Hz, 2H, chlorophenyl $H_{2,6}$). MS: *m/z* (%): 411 (100, $[M+1]^+$).

5.3.4. *3-(4-Bromophenyl)-5-(4-*n*-decyloxyphenyl)-pyrazole* (**2d**)

This compound was synthesized from 1-(4-bromophenyl)-3-(4-*n*-decyloxyphenyl)propan-1,3-dione (**1d**) using the same procedure as described for **2a**. Yield: 87%. IR, $\nu\,cm^{-1}$, NaCl: 3232 (NH), 1617, 1502 (pyrazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6.6$ Hz, 3H, $-CH_3$), 1·22–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·74–1·80 (m, 2H, $-O-CH_2-CH_2-$), 3·97 (t, $J = 6{\cdot}6$ Hz, 2H, $-OCH_2-$), 6·71 (s, 1H, $-CH=$), 6·92 (d, $J = 8{\cdot}7$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·50–7·56 (m, 4H, bromophenyl $H_{3,5}$ and decyloxyphenyl $H_{2,6}$), 7·47 (d, $J = 8{\cdot}5$ Hz, 2H, bromophenyl $H_{2,6}$). MS: *m/z* (%): 455 (100, $[M+1]^+$), 377 (38, $([M+1]-Br)^+$), 314 (35, $([M+1]-C_{10}H_{21})^+$).

5.3.5. *3-(4-Cyanophenyl)-5-(4-*n*-decyloxyphenyl)-pyrazole* (**2e**)

This compound was synthesized from 1-(4-cyanophenyl)-3-(4-*n*-decyloxyphenyl)propan-1,3-dione (**1e**) using the same procedure as described for **2a**. Yield: 70%. IR, $\nu\,cm^{-1}$, NaCl: 3224 (NH), 2224 (CN), 1610, 1506 (pyrazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}6$ Hz, 3H, $-CH_3$), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·76–1·81 (m, 2H, $-O-CH_2-CH_2-$), 3·98 (t, $J = 6{\cdot}5$ Hz, 2H, $-OCH_2-$), 6·78 (s, 1H, $-CH=$), 6·95 (d, $J = 8{\cdot}6$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·51 (d, $J = 8{\cdot}6$ Hz, 2H, decyloxyphenyl $H_{2,6}$), 7·68 (d, $J = 8{\cdot}3$ Hz, 2H, cyanophenyl $H_{3,5}$), 7·89 (d, $J = 8{\cdot}3$ Hz, 2H, cyanophenyl $H_{2,6}$). MS: *m/z* (%): 402 (100, $[M+1]^+$), 261 (42, $([M+1]-C_{10}H_{21})^+$).

5.4. *Synthesis of the isoxazoles*

5.4.1. *3-(4-*n*-Decyloxyphenyl)-5-phenylisoxazole* (**3a**)

A mixture of 1-(4-*n*-decyloxyphenyl)-3-phenylpropan-1,3-dione (**1a**) (0·4 mmol), hydroxylamine hydrochloride (25 mg, 0·4 mmol) and triethylamine (24 mg, 0·4 mmol) in ethanol (18 ml) was heated under reflux for 15 h and then stirred overnight at room temperature. The precipitated product was filtered off and recrystallized from ethanol. Yield: 70%. IR, $\nu\,cm^{-1}$, NaCl: 3133 (–CH= isoxazole), 1621, 1507 (isoxazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}6$ Hz, 3H, $-CH_3$), 1·26–1·47 (m, 14H, $-(CH_2)_7-CH_3$), 1·76–1·81 (m, 2H, $-O-CH_2-CH_2-$), 3·99 (t, $J = 6{\cdot}6$ Hz, 2H, $-OCH_2-$), 6·68 (s) and 6·76 (s) (1H, $-CH=$), 6·96 (d, $J = 8{\cdot}8$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·43–7·48 (m, 3H, unsub. phenyl $H_{3,5}$ and H_4), 7·76–7·86 (m, 4H, both aromatic rings $H_{2,6}$). MS: *m/z* (%): 378 (100, $[M+1]^+$), 261 (52, $C_{17}H_{25}O_2^+$), 238 (42, $([M+1]-C_{10}H_{21})^+$).

5.4.2. *3-(4-*n*-Decyloxyphenyl)-5-(4-methoxyphenyl)-isoxazole* (**3b**)

This compound was synthesized from 1-(4-*n*-decyloxyphenyl)-3-(4-methoxyphenyl)propan-1,3-dione (**1b**) using the same method as described for **3a**. Yield: 75%. IR, $\nu\,cm^{-1}$, NaCl: 3135 (–CH= isoxazole), 1616, 1510 (isoxazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}6$ Hz, 3H, $-CH_3$), 1·20–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·74–1·83 (m, 2H, $-O-CH_2-CH_2-$), 3·85 and 3·84 (2s, 3H, $-CH_3$), 3·99 (t, $J = 6{\cdot}5$ Hz, 2H, $-OCH_2-$), 6·63 (2s, 1H, $-CH=$), 6·94–6·99 (m, 4H, both aromatic rings $H_{3,5}$), 7·71–7·79 (m, 4H, both aromatic rings $H_{2,6}$). MS: *m/z* (%): 408 (100, $[M+1]^+$).

5.4.3. *3-(4-Chlorophenyl)-5-(4-*n*-decyloxyphenyl)-isoxazole* (**3c**)

This compound was synthesized from 1-(4-chlorophenyl)-3-(4-*n*-decyloxyphenyl)propan-1,3-dione (**1c**) using the same method as described for **3a**. Yield: 67%.

IR, $\nu\,cm^{-1}$, NaCl: 3132 (–CH= isoxazole), 1618, 1502 (isoxazole). ^1H NMR, δ ppm, $CDCl_3$: 0·87 (t, $J = 6{\cdot}6$ Hz, 3H, $-CH_3$), 1·26–1·47 (m, 14H, $-(CH_2)_7-CH_3$), 1·77–1·81 (m, 2H, $-O-CH_2-CH_2-$), 3·99 (t, $J = 6.6$ Hz, 2H, $-OCH_2-$), 6·65 (s) and 6·75 (s) (1H, –CH=), 6·97 (d, $J = 8{\cdot}8$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·43 (d, $J = 8{\cdot}6$ Hz) and 7·44 (d, $J = 8{\cdot}6$ Hz) (2H, chlorophenyl $H_{3,5}$), 7·72–7·79 (m, 4H, both aromatic rings $H_{2,6}$). MS: *m/z* (%): 412 (100, $[M+1]^+$).

5.4.4. *3 - (4 - Bromophenyl) - 5 - (4* - n - *decyloxyphenyl) - isoxazole* (**3d**)

This compound was synthesized from 1-(4-bromophenyl-3-(4-*n*-decyloxyphenyl)propan-1,3-dione (**1d**) using the same method as described for **3a**. Yield: 70%. IR, $\nu\,cm^{-1}$, NaCl: 3134 (–CH= isoxazole), 1620, 1499 (isoxazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}6$ Hz, 3H, $-CH_3$), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$), 1·76–1·81 (m, 2H, $-O-CH_2-CH_2-$), 3·99 (t, $J = 6{\cdot}6$ Hz, 2H, $-OCH_2-$), 6·65 (s) and 6·76 (s) (1H, –CH=), 6·96 (d, $J = 9{\cdot}2$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·59 (d, $J = 8{\cdot}3$ Hz) and 7·60 (d, $J = 8{\cdot}3$ Hz) (2H, bromophenyl $H_{3,5}$), 7·66–7·75 (m, 4H, both aromatic rings $H_{2,6}$). MS: *m/z* (%): 456 (100, $[M+1]^+$), 378 (50, $([M+1]-Br)^+$), 316 (41, $([M+1]-C_{10}H_{21})^+$).

5.4.5. *3 - (4 - Cyanophenyl) - 5 - (4* - n - *decyloxyphenyl) - isoxazole* (**3e**)

This compound was synthesized from 1-(4-cyanophenyl)-3-(4-*n*-decyloxyphenyl)propan-1,3-dione (**1e**) and hydroxylamine hydrochloride in equimolar quantities. The reaction mixture was heated under reflux for 32 h and then stirred at room temperature. The precipitated product was filtered off and recrystallized from ethanol and hexane. Yield: 50%, IR, $\nu\,cm^{-1}$, NaCl: 3124 (–CH= isoxazole), 2241 (CN), 1618, 1506 (isoxazole). ^1H NMR, δ ppm, $CDCl_3$: 0·86 (t, $J = 6{\cdot}6$ Hz, 3H, $-CH_3$), 1·26–1·45 (m, 14H, $-(CH_2)_7-CH_3$, 1·77–1·82 (m, 2H, $-O-CH_2-CH_2-$), 4·00 (t, $J = 6{\cdot}6$ Hz, 2H, $-OCH_2-$), 6·70 (s) and 6·88 (s) (1H, –CH=), 6·97 (d, $J = 8{\cdot}8$ Hz, 2H, decyloxyphenyl $H_{3,5}$), 7·72–7·78 (m, 4H, decyloxyphenyl $H_{2,6}$ and cyanophenyl $H_{3,5}$), 7·91 (d, $J = 8{\cdot}4$ Hz) and 7·95 (d, $J = 8{\cdot}4$ Hz) (2H, cyanophenyl $H_{2,6}$). MS: *m/z* (%): 403 (100, $[M+1]^+$), 262 (27, $C_{17}H_{25}O_2^+$).

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