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David H. Brown[a]; Peter Styring[a]
[a] Department of Chemical and Process Engineering, The University of Sheffield, Mappin St, Sheffield S1 3JD, UK,

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Synthesis, regioisomerism and characterization of unsymmetrical alkenyl-terminated isoxazole liquid crystals

DAVID H. BROWN and PETER STYRING*

Department of Chemical and Process Engineering, The University of Sheffield, Mappin St, Sheffield S1 3JD, UK

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Two series of unsymmetrical diphenyl-1,3-diketones, each species bearing one terminal alkene, have been synthesized. These diketones have been converted into their respective unsymmetrical diphenylisoxazoles [3(5)-(4-ω-alkenyloxyphenyl)-5(3)-(4-alkoxyphenyl)isoxazoles] which have been isolated as equal mixtures of two regioisomers, due to 3,5- and 5,3-substitution of the isoxazole ring. The mesogenic properties of the isoxazole liquid crystals have been studied by polarizing optical microscopy and DSC. The effect of increasing alkoxy chain length (C6–C10) on the properties of the two series of isoxazoles has been examined. The isoxazoles show enantiotropic smectic C, smectic A and nematic mesophases. A detailed ^{1}H and ^{13}C NMR spectroscopic study has examined both the 1,3-diketones and isoxazoles. Proximity of the terminal alkene to the diphenyl core can greatly affect the complexity of the ^{13}C NMR spectra.

1. Introduction

In the early 1990s there was a flurry of interest in isoxazole-based mesogens as calamitic liquid crystals. The reports in this area focused mainly on simple symmetrical bis-(4-alkoxyphenyl)- or bis-(4-alkenyloxyphenyl)-isoxazoles [1–5]. It was not until the late 1990s, with reports from Serrano and co-workers, that any studies were reported discussing unsymmetrical diphenyl-isoxazole liquid crystals [6, 7]. These reported unsymmetrical 3,5-diphenylisoxazole-based mesogens bearing an alkoxy chain at one end of the molecule and either polar groups (Cl, Br, CN) or chiral moieties at the other. Given the depth to which other classes of liquid crystals have been explored, structure–property relationships in isoxazole liquid crystals still remain fairly uncharted.

It is interesting to compare reports of the symmetrical bis-(4-alkoxyphenyl)- and bis-(4-alkenyloxyphenyl)-isoxazoles. While it is reported that the symmetrical alkoxy derivatives exhibit either smectic C and/or nematic mesophases, the alkenyloxy derivatives exhibit smectic A and/or nematic phases. The formation of the smectic A phase in the alkenyloxy derivatives could be due to the possible interdigitated packing of the alkenyl terminated mesogens. To date there have been no reports of unsymmetrical isoxazoles bearing both an alkoxy and an alkenyloxy chain. In fact, there appears to be a distinct lack of data on the effect of alkyl chain length on the properties of unsymmetrical diphenylisoxazole liquid crystals since the reports by Serrano and co-workers, which covered only the use of one length of alkyl chain.

As a prelude to studies of isoxazole-based liquid crystalline polymers and microsegregation phenomena using siloxanes, we report our initial studies into the monoalkenyl precursors, more specifically 3(5)-(4-ω-alkenyloxyphenyl)-5(3)-(4-alkoxyphenyl)isoxazoles, including the synthesis and characterization of two homologous series (see the scheme). These mesogens show enantiotropic smectic C, smectic A and nematic phases. Mesomorphic characteristics were studied by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). While previous studies into isoxazole liquid crystals have used ^{1}H NMR spectroscopy to examine the two possible isoxazole regioisomers (3,5- and 5,3-) obtained from the synthesis, in this study ^{1}H NMR alone proved inadequate due to the observed 'symmetry' in the core of the isoxazole. A detailed NMR examination, including ^{13}C NMR spectroscopy—an element of liquid crystal characterizations often overlooked—of the 1,3-diketone (**dk-*m*/*n***) and isoxazole (**I-*m*/*n***) series has indicated some interesting features with respect to the observed 'symmetry' of these unsymmetrical 1,3-diketones and isoxazoles and in the case of the isoxazoles, has confirmed the presence of regioisomers.

*Author for correspondence; e-mail: p.styring@sheffield.ac.uk

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2. Results and discussion

2.1. *Synthesis*

The synthesis of the unsymmetrical isoxazoles is outlined in the scheme. The 4-alkoxyacetophenones and ethyl 4-alkenyloxybenzoates were prepared from 4-hydroxyacetophenone and ethyl 4-hydroxybenzoate respectively, by reaction with the corresponding alkyl- or ω-alkenyl bromide, following standard procedures [8]. Reaction of the substituted acetophenones and ethyl benzoates with sodium hydride in dimethoxyethane [3, 8] afforded the unsymmetrical 1,3-diketone series **dk-*m*/*n*** ($m = 6, 11$; $n = 6$–10) in reasonable yield (33–52%). Subsequent reaction of the 1,3-diketones with hydroxylamine hydrochloride and triethylamine in ethanol, following standard procedures [3, 4, 6], resulted in the isolation of the isoxazole series **I-*m*/*n*** in high yield (74–94%), these being a mixture of two regioisomers, due to 3,5- and 5,3-substitution of the isoxazole ring. Not unsurprisingly the smaller isoxazoles and 1,3-diketones, **I-6/6**, **I-6/7**, **dk-6/6** and **dk-6/7**, yielded needle-like crystalline material upon recrystallization whereas for the large molecular species powders were isolated.

2.2. *NMR spectroscopy*

The ^{1}H NMR spectra of the 1,3-diketones exhibited features expected for these types of compounds. While this series of compounds are referred to as diketones, in d-chloroform solution they are predominantly in the keto–enol form (approx. 80%) (figure 1). All the spectra show a number of significant signals. A signal at 17 ppm due to the intramolecularly hydrogen-bonded OH of the keto–enol form, a singlet at 6.7 ppm due to the enol alkenyl hydrogen and a considerably smaller singlet at 4.5 ppm due to the methylene ($-COCH_2CO-$) protons of the residual diketone present. These features are characteristic of the solution keto–enol/diketone equilibrium.

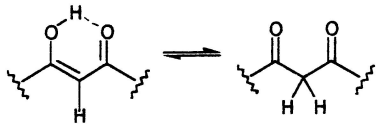
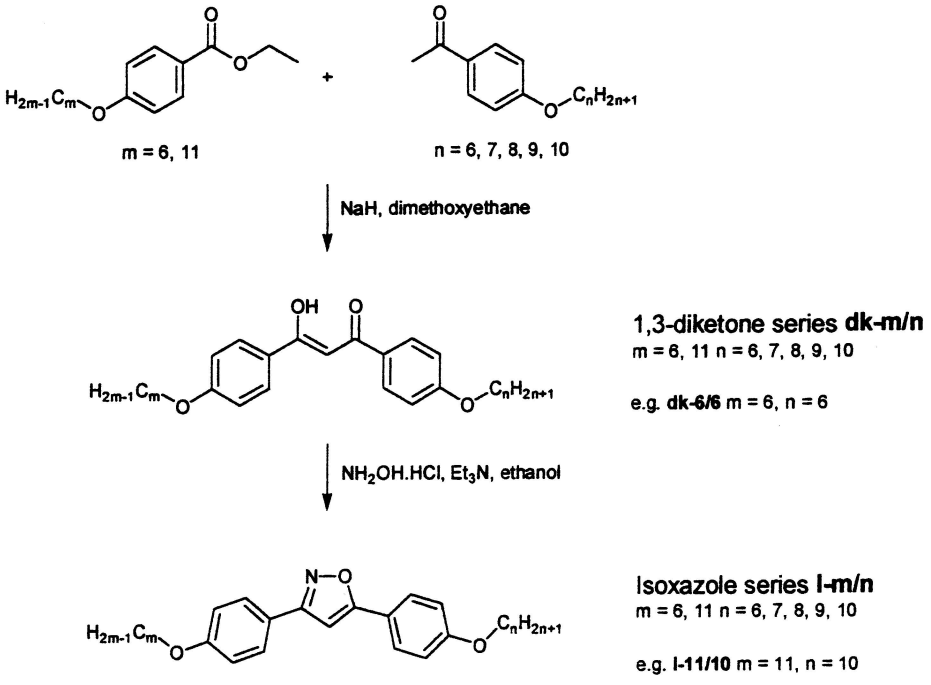


Figure 1. Keto-enol/diketone tautomerism.

It had been expected that the core of the compounds would appear 'symmetrical' due to the distance to the terminal units, however closer inspection of the ^{1}H and ^{13}C NMR spectra for the 1,3-diketone series revealed some interesting features with respect to this symmetry. Consider the two different interconverting tautomers of **dk-11/6** (A and B) and **dk-6/6** (C and D) in figure 2. The signals in the ^{1}H NMR spectra for **dk-11/6** (A and B) corresponding to 1 and 13 (plus 1′ and 13′) are coincident and show as a single triplet, but for **dk-6/6** (C and D) the chemical shifts for the signals for 1 and 13 are not coincident and thus show as two resolved triplets (2.5 Hz apart). This effect is due to proximity to the terminal groups of the chains. While this is not too surprising, the ^{13}C NMR spectra show even further 'long range' effects due to the terminal alkene in **dk-6/6**.



Scheme. Synthesis of a series of unsymmetrical 1,3-diketones and isoxazoles from ethyl alkenyloxybenzoates and alkoxyacetophenones.

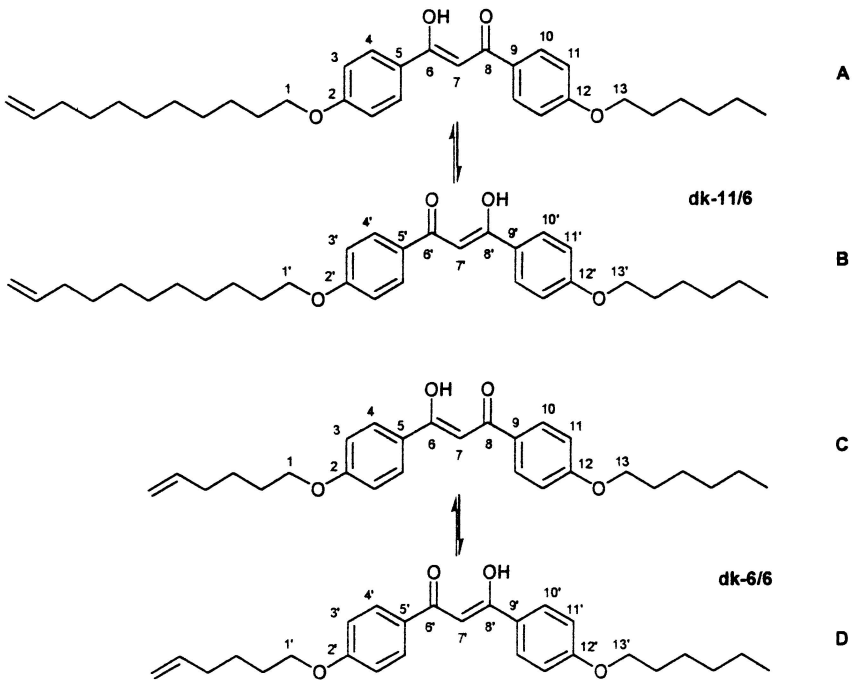


Figure 2. The keto–enol tautomers of **dk-11/6** (A and B) and **dk-6/6** (C and D).

Consider the structures A and C in figure 2. Each of them rapidly interconverts between the two different tautomers B and D respectively. For A, the ^{13}C NMR spectra is relatively simple. Amongst others, there are single signals at 184, 163, 128, 91 and 68 ppm. These signals correspond to carbons 6 and 8, 2 and 12, 5 and 9, 7, and 1 and 13 respectively. The signals corresponding to multiple 'different' carbons are coincident and show as a single peak. Of particular significance (for later arguments) is the coincidence of signals for 1 and 13, and 6 and 8. The signals for 6 and 8 appear as a single peak because of the averaging for signals for rapidly interconverting tautomers. The signal for 6 is in fact an average for the carbons 6 and 6′ on the two interconverting keto–enol tautomers and likewise for 8. In this case the average of 6/6′ and 8/8′ are coincident. Now consider structure C, in figure 2. In this case there are *two* closely spaced signals at 184 (3 Hz apart), 162 (5 Hz apart), 128 (4.5 Hz apart), and 68 ppm (16 Hz apart), corresponding to 6 and 8, 2 and 12, 5 and 9, and 1 and 13 respectively, but still only one signal at 91 ppm corresponding to 7. Why is this case so different? The difference arises because of the imposed 'lack of symmetry' due to the closeness of the alkenyl moiety. The signals for 1 and 13 are no longer coincident, as they were in A, neither are the signals for 2 and 12, and 5 and 9 (these are among the most obvious in the spectra). However the biggest surprise is the difference in 6 and 8. Again the signals corresponding to 6 and 8 are averages. The signal for 6 is the average of 6 and 6′ and 8 the average of 8 and 8′, but unlike in A the two average signals are *not* coincident. Presumably this is due to the position of the alkene in C compared with A. This is a rather astonishing observation given how far removed the alkenes are in each case.

The isoxazole series show a similar level of complexity in their NMR spectra. However in this case, instead of two species in equilibrium (diketone and keto–enol) and two rapidly converting keto–enol tautomers, each compound is in fact a mixture of two regioisomers. Due to the similarity of the two substituents on the 1,3-diketones, both being *4-alkoxyphenyl* groups, it was expected that the two regioisomers would form in equal amounts. It has been reported that when the substituents are significantly different (e.g. cyanophenyl instead of alkoxyphenyl) then there is discrimination in the reaction to form the isoxazole ring and the resulting regioisomers are produced in different amounts [6]. Generally the ^{1}H NMR spectra are relatively simple and have only a few points of interest. The spectrum for **I-11/6** (E and F in figure 3) shows only one singlet for the isoxazole CH (marked 7), the signals for the two regioisomers being coincident. Thus determination of relative proportions of the regioisomers from the ^{1}H NMR spectrum is not possible. The signals for 1 and 13 in E and F were coincident and appeared as a single triplet. The ^{13}C NMR spectrum for E and F (figure 3) is only slightly more complex. There is one signal for carbons 6 and 8′ (note: *not* 6 and 6′), one for 8 and 6′, two for the four carbons *ipso* to the phenolic oxygen (2, 12, 2′ and 12′) and two for the four aromatic carbons attached to the isoxazole ring (5, 9, 5′ and 9′), one for the isoxazole CH

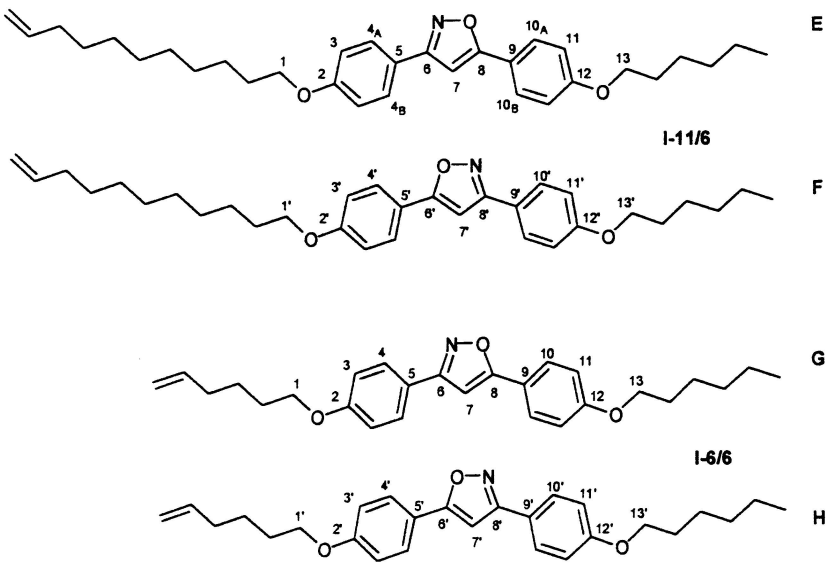


Figure 3. Regioisomers of **I-11/6** (E and F) and **I-6/6** (G and H).

(7 and 7′) but a complex pattern for the chain carbons 1, 13, 1′ and 13′ (each of the four carbons starting to appear separately). It is clear that the difference in the isoxazole ring (positions of N and O) affects the rest of the carbons in the diphenylisoxazole core. Essentially the two regioisomers E and F show an identical 'core' spectral pattern, i.e. the terminal substituents in the chains do not really affect the signals of the central carbons. This is not the case in **I-6/6**.

In the ^{1}H NMR spectrum of **I-6/6** (G and H in figure 3) there is only one obvious difference compared with **I-11/6** (E and F in figure 3). Like the 1,3-diketone analogue **dk-6/6**, the signals for 1 and 13 appear as two triplets (i.e. effects of terminal substituents). The differences in the ^{13}C NMR spectrum are more obvious. In this case (G and H) there are two signals for 6 and 8′, two for 8 and 6′, four for 2, 2′, 12 and 12′, four for the four alkenyl carbons, four for 5, 5′, 9, 9′, two for the isoxazole methyne carbons 7 and 7′ and four for 1, 13, 1′ and 13′. In fact almost *all* the carbons, except 4, 4′, 10 and 10′, and the two CH_2CH_3 groups, in G and H are separate (non-coincidental) signals. This is quite remarkable, especially considering the alkenes in G and H, the only difference being a *very* long range difference in the regioisomeric isoxazole ring. It has been reported by Chrisope *et al.* that long range effects in the diphenylisoxazole core can affect signals in the ^{13}C NMR spectrum, however the study was restricted only to changes in signals for the core carbons and did not include effects from further isolated substituents, such as the alkenyloxy groups in this case [9]. What the ^{13}C NMR spectrum does confirm, by way of similar intensities of signals, is that G and H are essentially in equal quantities in the mixture.

It should be noted that the spectral observations for the different compounds shown in figures 2 and 3, **dk-11/6**, **dk-6/6**, **I-11/6** and **I-6/6**, remain generally true for the rest of their series, i.e. the spectra for **dk-11/6**–**dk11/10**; **dk-6/6**–**dk-6/10**; **I-11/6**–**I-11/10** and **I-6/6**–**I-6/10** are roughly the same. Also, in the ^{13}C NMR spectra of the diketone series there are some signals corresponding to the diketones' tautomer, however they are insignificant compared with the rest of the visible signals.

2.3. *Mesomorphic properties*

The 1,3-diketone series **dk-*m*/*n*** did not exhibit liquid crystal properties. However this is not too unexpected given earlier studies of similar compounds showing that 1,3-diketones of this type do not form mesophases [3, 6, 8].

As expected, the isoxazoles in this study were found to be mesomorphic. The results of POM and DSC studies are summarized in table 1 and figure 4. All the isoxazoles exhibited enantiotropic nematic and smectic C phases, and the longer chained compounds exhibited additional smectic A phases. The shortest chained material of the series, **I-6/6**, displayed wide temperature range nematic (*c.* 30°C) and smectic C (*c.* 24°C) phases. Of all the isoxazoles studied **I-6/6** has the highest melting (102°C) and clearing (152°C) points. The phases were identified from their birefringence patterns by POM. The I–N transition wave front exhibited a schlieren pattern, however behind the transition front the nematic phases displayed a homeotropic texture, which was confirmed by its characteristic flashing and Brownian motion when pressure was applied to the cover slip. The smectic C showed a typical schlieren texture. As the length of the alkyl chain was extended from C_6 (in **I-6/6**)

Table 1. Optical, thermal and thermodynamic data for the isoxazole series (**I-*m*/*n***); temperatures (°C, derived from optical microscopy on cooling, unless otherwise stated)[c] and enthalpies (in brackets, kJ mol^{-1}, DSC cooling curve, ←(…)→ corresponds to the sum of multiple transitions).

Compound	Cr_1		Cr_2		SmC		SmA		N		I
I-6/6			•	98.0 (18.5)	•	122.1 (0.6)			•	152.1 (1.1)	•
I-6/7			•	88.9 (18.4)	•	127.7 (0.6)			•	150.0 (1.2)	•
I-6/8			•	76.8 (15.7)	•	132.0 (0.4)			•	149.2 (1.4)	•
I-6/9			•	70.2 (15.6)	•	131.5 (0.2)	•	134.0 ←	• (2.7)	145.7 →	•
I-6/10	•[a]	62.2[a] (16.2)	•	66.9 (15.4)	•	129.7 (n/a)[b]	•	134.0 (n/a)[b]	•	144.7 (n/a)[b]	•
I-11/6			•	71 (27.8)	•	136.1 (n/a)	•	144.7 ←	• (4.3)	150.1 →	•
I-11/7	•[a]	n/a ←	• (24.7)	71.9 →	•	140.3 (n/a)[b]	•	146.2 ←	• (4.5)	148.5 →	•
I-11/8			•	77.1 (19.8)	•	143.7 ←	• —	146.9 (6.1)	• —	149.5 →	•
I-11/9	•[a]	62.6[a] (26.4)	•	84.7 (23.2)	•	145.7 ←	• —	147.3 (6.6)	• —	148.6 →	•
I-11/10	•	79.7 (31.1)	•	89.3 (23.2)	•	147.5 ←	• —	148.5 (7.3)	• —	148.6 →	•

[a] Determined from a DSC cooling curve.
[b] Data could not be determined from DSC.
[c] Melting temperatures (Cr_2–SmC on heating) are as follows: **I-6/6** 101.8; **I-6/7** 93.5; **I-6/8** 78.6; **I-6/9** 74.1; **I-6/10** 74.5; **I-11/6** 78.5; **I-11/7** 78.1; **I-11/8** 80.7; **I-11/9** 87.1; **I-11/10** 94.7°C.

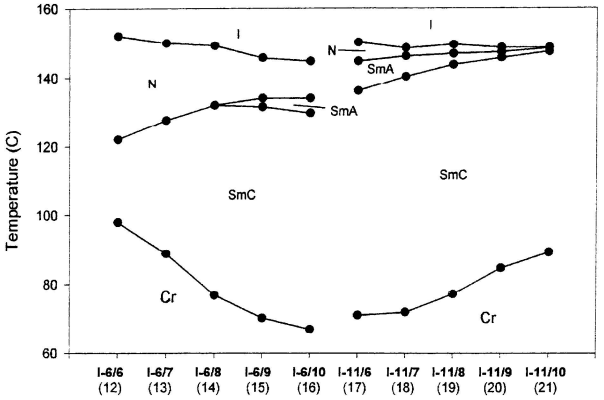


Figure 4. Phase transition temperatures for the isoxazole (**I-*m*/*n***) series. Number in brackets equals the total carbons in the chains (i.e. $m + n$).

to C_{10} (in **I-6/10**) the stability of the SmC phase increased, the N phase stability decreased, and the melting point (Cr–SmC) dramatically decreased as the compounds became less crystalline and packing less ordered. The first three in this series, **I-6/6**, **I-6/7** and **I-6/8**, exhibit only N and SmC phases but the larger homologues **I-6/9** and **I-6/10** also exhibit a SmA phase. The optical characteristics of the phase transitions and textures are virtually the same in these cases as with the shorter compounds. The SmA phase exhibited a homeotropic texture, which streaked but did not flash, unlike the N phase, when pressure was applied. Identification of the transition was fairly difficult for the homeotropic N to homeotropic SmA transition, except in this case there were defect regions in the homeotropic texture which exhibited a significant change at the transition temperatures. The two phases, before and after the transition, also responded differently to applied pressure, flashing and non-flashing (N and SmA).

The undecenyl isoxazole series **I-11/*n*** ($n = 6$–10) all showed the same phases, SmC, SmA and N. Again these phases were identified by their optical textures. The I–N transition showed a wave of schlieren texture going to a homeotropic N texture with schlieren regions. The SmA phase generally exhibited a homeotropic texture with small region of focal-conic texture and the majority of the SmC phase showed typical schlieren textures. As the length of the alkyl chain increased from C_6 (**I-11/6**) to C_{10} (**I-11/10**) the SmC phase stability remained approximately the same (58 to 65°C) whereas the stability of

the N phase (5 to 0.1°C) and SmA phase (9 to 1°C) decreased markedly. At the same time the crystallization points increased significantly (71 to 89°C). The increase in melting points is due to the effect of increasing molecular mass of the species, rather than a better packing effect. For longer homologues (**I-11/10**) there is essentially only a SmC phase with the SmA phase stable only for *c.* 1°C and the nematic phase only existing momentarily in the wave front of a I–N–SmA transition.

Generally all the isoxazoles have a similar clearing point, within *c.* 7°C. Overall there is only a small 'odd–even' effect, noticeably in the clearing point of the **I-11/*n*** series, but this is essentially insignificant.

A summary of the data from DSC studies is listed in table 1. The DSC thermograms were straight-forward for the smallest isoxazoles **I-6/6**, **I-6/7** and **I-6/8**, i.e. the compounds that showed only SmC and N mesophases. The thermograms show distinct sharp, separate signals that coincide with the phase transitions observed optically. However for the compounds that also exhibit SmA phases, the thermograms are more complex. The narrow temperature range over which some of the phases are stable leads to overlapping signals. In many cases, as indicated in table 1, transition enthalpies could only be determined for multiple transitions. This is especially the case for **I-11/7**–**I-11/10** where the I–N–SmA–SmC transitions are very narrow, resulting in overlapping signals in the DSC thermograms. In some cases second order phase transitions prevented the determination of transition enthalpies, especially for the weak SmA–SmC transitions. The transition enthalpies show a few trends. As the series increases in length from **I-6/6**, the enthalpy of melting (Cr–SmC) initially decreases. This is representative of the increasing ease of melting as the solid state packing is disrupted by further increasing chain lengths, when comparing the obviously crystalline **I-6/6** and **I-6/7** (recrystallized as needles) with the longer compounds in the series. Another obvious trend is the increase in the 'total clearing' enthalpies (i.e. the sum of all enthalpies of transition from SmC to I phase). For example the total for the transition SmC–N–I for **I-6/6** is 1.7 kJ mol^{-1} whereas for **I-11/10** the total for the SmC–SmA–N–I transition is 7.3 kJ mol^{-1}. This is because of the increasing attractive forces as the molecules become larger, and so more energy is required to take the species into the isotropic phase.

3. Conclusions

We report the synthesis and characterization of two homologous series of 1,3-diketones and isoxazoles that are unsymmetrical, containing one terminal alkyl group and one terminal alkenyl group each. The unsymmetrical nature of these compounds results in some complicated ^{13}C NMR spectra when the alkenyl group is closer to the diphenyl-1,3-diketone or -isoxazole core. The isoxazoles are prepared as a one to one mixture of two regioisomers 3,5- and 5,3- as shown by the ^{1}H and ^{13}C NMR spectra.

The unsymmetrical isoxazoles from this study exhibit smectic C and nematic phases for the shortest of the series but also exhibit smectic A phases as the chain lengths on the alkenyl and alkyl substituents increase. This compares to previous studies of symmetrical diphenylisoxazoles, those bearing just alkyloxy substituents exhibited smectic C and nematic phases whereas those with just alkenyloxy substituents exhibited smectic A and nematic phases. In this study with unsymmetrical substituents, one alkyloxy and one alkenyloxy group, we observe both smectic A and smectic C mesomorphism. We are now undertaking studies into the effect of further functionalizing the alkenyl group, by addition of a siloxyl moiety.

4. Experimental

4.1. *General*

1,2-Dimethoxyethane was dried over 4 Å molecular sieves. The 4-*n*-alkoxyacetophenones (C6–C10) were prepared according to literature methods [8]. The ethyl 4-*n*-alkenyloxybenzoates were prepared by an analogous method, their NMR spectra being consistent with the literature [10, 11].

NMR spectra were recorded using a Bruker AC250 spectrometer (^{1}H, 250.1 MHz, ^{13}C 62.9 MHz). ^{1}H and ^{13}C chemical shifts were referenced to solvent resonances. For the microanalyses a Perkin Elmer 2400 CHN Elemental Analyser was used. The thermal behaviour of the materials was studied using a polarizing optical microscope equipped with a Linkam TH600 microfurnace and PR600 controller unit (heating rate 2°C min^{-1} near phase changes). Phases transitions were confirmed by DSC using a Perkin Elmer Pyris 1 at a scan rate of 10° min^{-1}.

4.2. *Synthesis of the 1,3-diketone series*

4.2.1. *1-(4-Undec-10′-enyl-1′-oxyphenyl)-3-(4′-hexyl-1′-oxyphenyl)propane-1,3-dione (**dk-11/6**)*

A solution of 4-hexyloxyacetophenone (1.1 g, 5 mmol) in dimethoxyethane (25 ml) was added to sodium hydride (60%, 0.5 g, 12 mmol; pre-washed in light petrol). To this stirred suspension was added a solution of ethyl 4-undec-10′-enyloxybenzoate (1.6 g, 5 mmol) in dimethoxyethane (25 ml). The resulting mixture was heated under reflux for 6 h. After cooling, water (2 ml) was added, and the mixture acidified to approx. pH 2 using hydrochloric acid (20%) and then extracted with diethyl ether (50 ml).

The organic phase was separated, washed with water (2×20 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The resulting solid was recrystallized from ethanol to yield a yellow solid (0.84 g, 34%).

All the compounds in this series were prepared by a similar method. Yields, mass spectra, microanalysis data and melting points are shown in table 2. Typical NMR spectral analyses are given below for the two series ($m = 6$ and 11 in scheme 1).

4.2.2. *1-(4-Undec-10′-enyl-1′-oxyphenyl)-3-(4′-hexyl-1′-oxyphenyl)propane-1,3-dione (**dk-11/6**)*

^{1}H NMR ($CDCl_3$; 250 MHz): 0.91 (3H, t, $J = 7$ Hz, $-CH_3$), 1.23–1.55 (18H, m, $-CH_2(CH_2)_6CH_2CH{=}CH_2$ and $-(CH_2)_3CH_3$), 1.80 (4H, m, $2 \times -OCH_2CH_2-$), 2.04 (2H, m, $-CH_2CH{=}CH_2$), 4.00 (4H, t, $J = 6.5$ Hz, $2 \times -OCH_2-$), 4.51 (< 18%, s, $-COCH_2CO-$), 4.90–5.03 (2H, m, $-CH{=}CH_2$), 5.81 (1H, m, $-CH{=}CH_2$), 6.72 (1H, s, $-COCH{=}COH-$enol), 6.94 (4H, AA′ part of AA′XX′ pattern, aromatic H 3/5 *ortho* to phenolic carbon), 7.93 (4H, XX′ part of AA′XX′ pattern, aromatic H 2/6 *meta* to phenolic carbon) and 17.18 (1H, s, −OH enol).

^{13}C NMR ($CDCl_3$; 62.9 MHz): 14.0 ($-CH_3$), 22.6 ($-CH_2CH_3$), 25.6, 26.0, 28.9, 29.08 br, 29.1, 29.3, 29.4, 29.5, 31.5 ($-OCH_2(CH_2)_3CH_2CH_3$ and $-OCH_2(CH_2)_7CH_2CH{=}CH_2$), 33.8 ($-CH_2CH{=}CH_2$), 68.2 ($2 \times -OCH_2-$), 91.3 ($-COCH{=}COH-$), 114.1 ($-CH{=}CH_2$), 114.3 (CH, Ar, *ortho* to phenolic carbon), 127.9 (C, Ar, *para* to phenolic carbon), 129.0 (CH, Ar, *meta* to phenolic carbon), 131.3 (trace, CH, Ar of diketone form), 139.2 ($-CH{=}CH_2$), 162.6 (C, Ar, phenolic carbon) and 184.5 ($-COCH{=}COH-$).

4.2.3. *1-(4-Hex-5-enyloxyphenyl)-3-(4-hexyl-1-oxyphenyl)propane-1,3-dione (**dk-6/6**)*

^{1}H NMR ($CDCl_3$; 250 MHz): 0.91 (3H, t, $J = 6.9$ Hz, $-CH_3$), 1.25–1.68 (8H, m, $-CH_2CH_2CH{=}CH_2$ and $-(CH_2)_3CH_3$), 1.81 (4H, m, $2 \times -OCH_2CH_2-$), 2.13 (2H, m, $-CH_2CH{=}CH_2$), 4.00 (2H, t, $J = 6.5$ Hz, $-OCH_2-$), 4.02 (2H, t, $J = 6.4$ Hz, $-OCH_2-$), 4.50 (< 20%, s, $-COCH_2CO-$), 4.94–5.08 (2H, m, $-CH{=}CH_2$), 5.83 (1H, m, $-CH{=}CH_2$), 6.72 (1H, s, $-COCH{=}COH-$enol), 6.94 (4H, AA′ part of AA′XX′ pattern, aromatic H 3/5 *ortho* to phenolic carbon), 7.93 (4H, XX′ part of AA′XX′ pattern, aromatic H 2/6 *meta* to phenolic carbon) and 17.18 (1H, s, −OH enol).

^{13}C NMR ($CDCl_3$; 62.9 MHz): 14.0 ($-CH_3$), 22.6 ($-CH_2CH_3$), 25.2, 25.6, 28.5, 29.1, 31.5 ($-OCH_2-(CH_2)_3CH_2CH_3$ and $-OCH_2(CH_2)_2CH_2CH{=}CH_2$), 33.4 ($-CH_2CH{=}CH_2$), 68.0, 68.2 ($2 \times -OCH_2-$), 91.3 ($-COCH{=}COH-$), 114.31, 114.32 (CH, Ar, *ortho* to phenolic carbon), 114.8 ($-CH{=}CH_2-$), 127.8, 127.9 (C, Ar, *para* to phenolic carbon), 129.0 (CH, Ar, *meta* to phenolic carbon), 131.3 (trace, CH, Ar of diketone form), 139.2 ($-CH{=}CH_2$), 162.5, 162.6 (C, Ar, phenolic carbon) and 184.5, 184.55 ($-COCH{=}COH-$).

4.3. *Synthesis of the isoxazole series*

4.3.1. *3(5)-(4-Undec-10′-enyl-1′-oxyphenyl)-5(3)-(4-hexyl-1′-oxyphenyl)isoxazole (**I-11/6**)*

A mixture of 1-(4-undec-10′-enyloxyphenyl)-3-(4-hexyloxyphenyl)propane-1,3-dione (0.77 g, 1.6 mmol), hydroxylamine hydrochloride (0.80 g, 11 mmol) and triethylamine (0.7 ml, 7 mmol) in ethanol (15 ml) was heated at reflux for 2.5 h. Additional hydroxylamine hydrochloride (0.4 g, 6 mmol) was added to the mixture which was then heated at reflux for a further 2.5 h. The mixture was allowed to stand overnight and the precipitate was collected. The solid was dissolved in dichloromethane (15 ml). The organic phase was washed with water (5 ml), dried ($MgSO_4$ and K_2CO_3) and evaporated to dryness. The residue was recrystallized from ethanol (*c.* 30 ml) to yield a white solid (0.53 g, 68%).

All the compounds in this series were prepared by a similar method. Yields, mass spectra, microanalysis data and mesomorphic properties are shown in tables 1 and 3. Typical NMR spectral analyses are given below for the two series ($m = 6$ and 11 in scheme 1).

Table 2. Analytical data for the 1,3-diketone series (**dk-*m*/*n***).

Compound	Yield/%	M.p./°C	%C found (calc.)	%H found (calc.)	Mass spectrometry
dk-6/6	46	67–70	76.86 (76.74)	8.17 (8.11)	422 (M+, 100%), 205, 203, 121
dk-6/7	48	69–71	77.09 (77.03)	8.51 (8.31)	436 (M+, 100%), 219, 203, 121
dk-6/8	33	66–67	77.16 (77.30)	8.63 (8.50)	450 (M+, 100%), 233, 203, 121
dk-6/9	41	59–62	77.77 (77.55)	8.88 (8.68)	464 (M+, 100%), 247, 203, 121
dk-6/10	41	58–63	77.81 (77.79)	8.95 (8.84)	478 (M+, 100%), 261, 203, 121
dk-11/6	34	66–68	78.21 (78.01)	9.06 (9.00)	492 (M+), 273, 205, 121 (100%)
dk-11/7	36	66–68	78.33 (78.22)	9.06 (9.15)	506 (M+), 273, 219, 121 (100%)
dk-11/8	40	71–73	78.66 (78.42)	9.37 (9.29)	520 (M+, 100%), 273, 233, 121
dk-11/9	46	76–78	78.77 (78.61)	9.51 (9.42)	534 (M+, 100%), 273, 247, 121
dk-11/10	52	81–84	79.01 (78.79)	9.61 (9.55)	548 (M+, 100%), 273, 261, 121

Table 3. Analytical data for the isoxazole series (**I-*m*/*n***).

Compound	Yield/%	%C found (calc.)	%H found (calc.)	%N found (calc.)	Mass spectrometry
I-6/6	74	77.48 (77.29)	8.11 (7.93)	3.18 (3.34)	419 (M+), 337, 253, 121 (100%)
I-6/7	84	77.45 (77.56)	8.20 (8.14)	3.35 (3.23)	433 (M+), 351, 253, 121 (100%)
I-6/8	94	77.60 (77.82)	8.41 (8.33)	3.18 (3.13)	447 (M+), 365, 253, 121 (100%)
I-6/9	90	78.13 (78.05)	8.76 (8.52)	3.02 (3.03)	461 (M+, 100%), 379, 253, 121
I-6/10	77	78.40 (78.28)	8.97 (8.69)	2.82 (2.94)	475 (M+, 100%), 393, 253, 121
I-11/6	68	78.64 (78.49)	8.95 (8.85)	2.76 (2.86)	490 (M + 1, 100%), 337, 253, 121
I-11/7	80	78.89 (78.69)	9.09 (9.00)	2.69 (2.78)	504 (M + 1, 100%), 351, 253, 121
I-11/8	85	78.97 (78.87)	9.07 (9.15)	2.56 (2.71)	518 (M + 1, 100%), 365, 253, 121
I-11/9	82	79.07 (79.05)	9.36 (9.29)	2.55 (2.63)	531 (M+, 100%), 379, 253, 121
I-11/10	83	79.31 (79.22)	9.37 (9.42)	2.47 (2.57)	545 (M+, 100%), 393, 253, 121

4.3.2. *3(5)-(4-Undec-10′-enyl-1′-oxyphenyl)-5(3)-(4-hexyl-1′-oxyphenyl)isoxazole (**I-11/6**)*

^{1}H NMR ($CDCl_3$; 250 MHz): 0.90 (3H, t, $J = 6.5$ Hz, $-CH_3$), 1.24–1.51 (18H, m, $-CH_2(CH_2)_6CH_2CH{=}CH_2$ and $-(CH_2)_3CH_3$), 1.79 (4H, m, $2 \times -OCH_2CH_2-$), 2.03 (2H, m, $-CH_2CH{=}CH_2$), 3.98 (4H, t, $J = 6.6$ Hz, $2 \times -OCH_2-$), 4.89–5.03 (2H, m, $-CH{=}CH_2$), 5.80 (1H, m, $-CH{=}CH_2$), 6.62 (1H, s, isoxazole CH), 6.95 (4H, m/apparent d, aromatic H 3/5 *ortho* to phenolic carbon) and 7.74 (4H, m/apparent t, aromatic H 2/6 *meta* to phenolic carbon).

^{13}C NMR ($CDCl_3$; 62.9 MHz): 14.0 ($-CH_3$), 22.6 ($-CH_2CH_3$), 25.67, 25.69, 25.98, 25.99, 28.9, 29.09, 29.11, 29.13, 29.15, 29.18, 29.27, 29.33, 29.35, 29.4, 29.5, 31.55, 31.56 ($-OCH_2(CH_2)_3CH_2CH_3$ and $-OCH_2(CH_2)_7CH_2CH{=}CH_2$), 33.8 ($-CH_2CH{=}CH_2$), 68.08br, 68.13, 68.15 ($2 \times -OCH_2-$), 95.8 (isoxazole CH), 114.1 ($-CH{=}CH_2$), 114.74, 114.8 (CH, Ar, *ortho* to phenolic carbon), 120.1, 121.5 (C, Ar, *para* to phenolic carbon), 127.3, 128.1 (CH, Ar, *meta* to phenolic carbon), 139.2 ($-CH{=}CH_2$), 160.5, 160.6 (C, Ar, phenolic carbon), 162.5 (C3 isoxazole) and 170.1 (C5 isoxazole).

4.3.3. *3(5)-(4-Hex-5′-enyl-1′-oxyphenyl)-5(3)-(4-hexyl-1′-oxyphenyl)isoxazole (**I-6/6**)*

^{1}H NMR ($CDCl_3$; 250 MHz): 0.90 (3H, t, $J = 6.9$ Hz, $-CH_3$), 1.34 (4H, m), 1.45 (2H, m), 1.56 (2H, m) ($-CH_2CH_2CH{=}CH_2$ and $-(CH_2)_3CH_3$), 1.80 (4H, m, $2 \times -OCH_2CH_2-$), 2.12 (2H, m, $-CH_2CH{=}CH_2$), 3.98 (2H, t, $J = 6.6$ Hz, $-OCH_2-$), 3.99 (2H, t, $J = 6.4$ Hz, $-OCH_2-$), 4.94–5.08 (2H, m, $-CH{=}CH_2$), 5.82 (1H, m, $-CH{=}CH_2$), 6.62 (1H, s, isoxazole CH), 6.95 (4H, m/apparent d, aromatic H 3/5 *ortho* to phenolic carbon) and 7.74 (4H, m/apparent t, aromatic H 2/6 *meta* to phenolic carbon).

^{13}C NMR ($CDCl_3$; 62.9 MHz): 14.0 ($-CH_3$), 22.6 ($-CH_2CH_3$), 25.25, 25.27, 25.66, 25.68, 28.57, 28.62, 29.11, 29.15, 31.54, 31.55 ($-OCH_2(CH_2)_3-CH_2CH_3$ and $-OCH_2(CH_2)_2CH_2CH{=}CH_2$), 33.37, 33.39 ($-CH_2CH{=}CH_2$), 67.84, 67.90, 68.09, 68.16 ($2 \times -OCH_2-$), 95.77, 95.79 (isoxazole CH), 114.75, 114.76, 114.83 br (CH, Ar, *ortho* to phenolic carbon), 114.78, 114.81 ($-CH{=}CH_2$), 120.14, 120.20, 121.52, 121.60 (C, Ar, *para* to phenolic carbon), 127.3, 128.1 (CH, Ar, *meta* to phenolic carbon), 138.38, 138.43 ($-CH{=}CH_2$), 160.43, 160.51, 160.56, 160.64 (C, Ar, phenolic carbon), 162.52, 162.54 (C3 isoxazole) and 170.10, 170.14 (C5 isoxazole).

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