Synthesis, characterisation and mesomorphic behaviours of non-symmetrically substituted 1,2,4- and 1,3,4-oxadiazole derivatives

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ABSTRACT

Two series of non-symmetrically substituted bent-core mesogens derived from the central 3,5 and 2,5 cores of the 1,2,4- and 1,3,4-oxadiazole derivatives, respectively, containing ether and ester linkage have been synthesised by several straightforward synthetic procedures, and their mesomorphic behaviour was studied by optical polarising microscopy (OPM) and differential scanning calorimetry (DSC). The last five homologues of the 1,2,4-oxadiazole series exhibit a monotropic nematic phase on cooling, while the 1,3,4-oxadiazole derivatives do not show any liquid crystalline properties but rather a crystal to isotropic transition is observed by OPM. We show that the bent angles of the 1,2,4- and 1,3,4-oxadiazole rings are crucial in observing the liquid crystal (LC) phases formed, and also that the length of the alkyl substituent is observed to have a significant effect on the nature of the LC phases.

1. Introduction

Mesogens or liquid crystal (LC) materials have wide technical applications in the device and display industry. In addition, these materials are used in many new fields such as organic light-emitting diodes, biosensors, field-effect transistors, anisotropic networks and various biological applications [1,2].

Bent-shaped or banana-shaped materials, also known as boomerangs or bows, have developed into a very promising area for new mesogens since 1970 [3]. Many banana-shaped materials have been reported [4–6], and the first bent-core 2,5-diphenyl-1,3,4-oxadiazoles with two additional benzene rings, representing bent-core mesogens, were reported by Semmler et al. [7]. The dependence between chemical composition and LC behaviour is one of the important problems in the field of mesogenic materials, and comprehensive studies have been carried out to understand the relationship between structure and property in bent-shaped mesogenic cores [8,9].

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The insertion of heterocyclic rings as core moieties in LCs causes large changes in their mesomorphism and physical properties because they then possess a greater number of polarisable heteroatoms such as N, O and S atoms [10,11].

Usually five- or six-membered heterocyclic rings are involved, and they form part of many types of cores, such as rod-, bent- and disc-shaped molecules [12].

In recent years, the 1,2,4- and 1,3,4-oxadiazole-based mesogens have been paid much attention, because certain kinds of these derivatives exhibit mesomorphic behaviours with various LC phases, especially the 1,3,4-oxadiazoles [13,14]. The first liquid crystalline 1,3,4-oxadiazoles were reported by Girdziunaite et al. [15]. In addition, Torgova et al. [16] synthesised a variety of mesogenic 1,2,4-oxadiazoles and, furthermore, many examples of this type of structure have been reported in the literature [17–19].

The 1,2,4-oxadiazole ring has similar luminescence and thermal stability properties to the 1,3,4-isomers, but for compounds containing the 1,2,4-oxadiazole ring their mesomorphic properties have not been studied extensively [16] because the asymmetric ring and the high dipole between the O and N atoms lead to different effects than those shown by the 1,3,4-isomers in the liquid crystalline phases.

The main aim of this work was to synthesise two series of oxadiazole derivatives with the same structure, but differing only in the oxadiazole ring, with 1,2,4- and 1,3,4-isomers. A comparative study was then undertaken of their liquid crystalline properties and the relationship of the two oxadiazole isomers to the resultant mesomorphic properties.

2. Experimental section

For all experimental details, see the supplementary material available via the multimedia link on the online article webpage.

3. Results and discussion

3.1. Synthesis

The synthetic routes for the preparation of compounds [F$_1$–F$_{11}$] and [K$_1$–K$_{11}$] are outlined in Schemes 1 and 2, respectively.

All of the synthesised compounds gave satisfactory analysis for the proposed structures, which were confirmed on the basis of their Fourier transform-infrared (FT-IR) elemental analysis, and some of them by mass spectroscopy and $^1$H nuclear magnetic resonance (NMR) (see the experimental details given in the supplementary material). Most of the intermediate compounds in this study were prepared according to the procedures in our references [20,21] with a few simple modifications; also, the compounds A and B were prepared based on the methods described in the references [22] and [23], respectively. The first step in Scheme 1 is the synthesis of compound A by the standard esterification method of 4-methylbenzoic acid. The reaction of compound A with hydrazine hydrate 80% in ethanol

![Scheme 1](image-url)
leads to the formation of hydrazide B. Compound C was then synthesised by the alkylation reaction of 4-hydroxybenzoic acid with 1-bromobutane in alkali aqueous methanolic solution. The condensation reaction between hydrazide B and 4-butoxybenzoic acid C in phosphorusoxy chloride leads to the formation of 2-(4-butoxyphenyl)-5-(p-tolyl)-1,3,4-oxadiazole D. The acid derivative 4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoic acid E was obtained by permanganate oxidation of component D in the mixed pyridine–water solution. Then the 1,3,4-oxadiazole derivatives F1–F11 were obtained by O-acylation of ROH with benzoic acid E with about 57–67% yields, using DCC as a condensation agent and catalytic quantities of DMAP. The aliphatic protons in 1H-NMR and FT-IR data and also the carbonyl of the esters F1–F11 near 1716–1722 cm⁻¹ were utilised to confirm the esterification of the carboxy group in compound E. Figure S1 in the supplementary material shows the 1H-NMR spectra for compounds F2 and F11 as examples of the compounds F1–F11.

3.2. Mesomorphic behaviours

3.2.1. Mesomorphic behaviours of compounds F1–F11

The mesomorphic properties of compounds F1–F11 were studied by optical polarising microscopy (OPM). These compounds did not show mesomorphic behaviours and only the crystal to isotropic transition was observed (Cr–I). The transition temperatures from the first heating scans in OPM for all compounds have been listed in Table 1. A plot of the crystal to isotropic transition temperatures as a function of the length of the terminal alkoxy chain for these compounds is shown in Figure S3. This figure shows a smooth falling tendency in the crystal to isotropic transition. However, the isotropic temperatures of these compounds decrease in a slightly similar odd–even order.

| Compound | Cr | I |
|----------|----|---|
| F1       | 145|   |
| F2       | 116|   |
| F3       | 133|   |
| F4       | 127|   |
| F5       | 120|   |
| F6       | 101|   |
| F7       | 98 |   |
| F8       | 99 |   |
| F9       | 88 |   |
| F10      | 101|   |
| F11      | 103|   |
3.2.2. Mesomorphic behaviours of compounds K₁−K₁₁.

The liquid crystalline properties of compounds K₂−K₁₁ were studied by OPM and differential scanning calorimetry (DSC), while only OPM was used to study the liquid crystalline behaviour of the compounds K₁−K₆. Table 2 shows the transition temperatures from crystal to isotropic phase for compounds K₁−K₆. The phase transition temperatures observed by OPM agree well with the corresponding DSC thermograms. The phase transition temperatures (T°C), phase transition enthalpy changes (ΔH/kJ mol⁻¹) and entropies (ΔS/J mol⁻¹ K⁻¹) were determined by DSC in the first heating and cooling scans for compound K₇−K₁₁ and have been listed in Table 3.

As can be seen from Tables 2 and 3, the first six homologues K₁−K₆ exhibit no mesomorphic phase and only a crystal to isotropic transition was observed on OPM, while compounds K₇−K₁₁ exhibit monotropic mesomorphic behaviour only on cooling.

3.2.2.1. DSC studies. The DSC thermographs of compounds K₁, K₉ and K₁₀ show only one transition on first heating (Cr–I), while the homologues K₈ and K₁₁ exhibit two transitions on first heating (Cr–Cr₁) and (Cr₁–I). On first cooling from the isotropic phase for compounds K₇−K₁₁, only two transitions were observed, which correspond to the isotropic–nematic (I–N) and nematic–crystalline (N–Cr) transitions. Therefore, the last five compounds of this series are monotropic mesogens. Figure S4 shows the DSC thermographs of homologues K₇−K₁₁.

3.2.2.2. OPM studies. Only the nematic phase was observed from textural observation by thermal microscopy under OPM for derivatives K₇−K₁₁ on cooling, and this in these showed a characteristic Schlieren texture, which appears in a very narrow temperature range. A plot of transition temperature on cooling against the number of carbon atoms in the ester linkage chain is shown in Figure S5 for compounds K₇−K₁₁. An increase in ester terminal length is often helpful to enhance the dipole–dipole interaction between the terminal chains and to facilitate the formation of the nematic phase. Figure S6 and Figure 1 show polarising optical photomicrographs of some compounds in this series.

If we compare the chemical structure of compounds F₁−F₁₁ with that of compounds K₁−K₁₁, the only difference is related to the central heterocyclic ring, 1,3,4-oxadiazole and 1,2,4-oxadiazole, respectively. Thus, the liquid crystalline properties are very strongly affected by the types of oxadiazole isomers as a core in the molecule. The last five compounds of the 1,2,4-oxadiazole series K₇−K₁₁ are mesogens with a nematic texture while all compounds of the 1,3,4-oxadiazole series F₁−F₁₁ are non-mesogenic compounds. This should mainly be due to the deviation from the rod-like molecular shape, with the difference between the two isomers (2,5-disubstituted-1,3,4-oxadiazole and 3,5-disubstituted-1,2,4-oxadiazole) being the exocyclic bond angle, 134° for the first isomer and 140° for the second isomer.[24,25]see Scheme 3.

The 1,3,4-isomer has a slightly lower bond angle [26], which is due to the position of the heteroatoms (O and N). In the two isomers of the oxadiazoles, the deviation from a typical calamitic mesogen symmetry towards a non-linear shape could clarify the disappearance of the mesomorphic properties in compounds F₁−F₁₁. These compounds may be giving mesomorphic properties if introduced into another

| Table 2. Crystal (Cr) to isotropic (I) transition temperatures (°C) from the first heating scan in OPM for compounds K₁−K₆. |
|----------|-----|-----|
| Compound | Cr  | I   |
| K₁       | 93  |     |
| K₂       | 98  |     |
| K₃       | 118 |     |
| K₄       | 113 |     |
| K₅       | 96  |     |
| K₆       | 87  |     |

| Table 3. Phase transition temperatures (T°C), phase transition enthalpy changes (ΔH/kJ mol⁻¹) and entropies (ΔS/J mol⁻¹ K⁻¹) of compounds K₂−K₁₁ in the first heating and cooling cycles. |
|----------|-----|-------------------------------|-------------------------------|
| Compound | n   | Phase transition T°C (ΔH/kJ mol⁻¹) | Phase transition T°C (ΔH/kJ mol⁻¹) |
|          |     | on first heating | on first cooling |
| K₁       | 7   | Cr−I 82.15 (34.81) [98.01] | I−N 68.80 (−0.39) [−1.14] |
| K₂       | 8   | Cr−Cr₁ 76.95 (1.78) [5.09] | N−Cr 60.00 (−18.39) [−55.23] |
| K₃       | 9   | Cr−I 82.05 (8.91) [25.09] | I−N 64.50 (−0.18) [−0.49] |
| K₄       | 10  | Cr−I 83.45 (30.91) [86.72] | N−Cr 52.35 (−9.38) [−28.83] |
| K₅       | 10  | Cr−I 76.25 (33.25) [95.20] | I−N 68.00 (−0.40) [−1.17] |
| K₆       | 12  | Cr−Cr₁ 79.20 (7.14) [20.27] | N−Cr 52.30 (−24.22) [−74.46] |
| K₇       |     | Cr−I 85.10 (11.25) [31.42] | I−N 65.45 (−0.34) [−0.99] |

Cr, Cr₁, Cr₂: crystal phase; N: nematic phase; I: isotropic phase.
phenyl group or aromatic heterocyclic ring at the end of one of the alkyl chains in the molecules, and this is what will be done in a new study in the near future. After reviewing the literature, we found that the results obtained in this study were fully compliant with the results by Parra et al. However, most of the studied 1,2,4-oxadiazole derivatives were mesogens rather than 1,3,4-oxadiazole derivatives, which have the same structure.

4. Conclusion

Two series of ester compounds based on the two isomers of the oxadiazole ring have been synthesised and characterised, and the last five compounds of the 1,2,4-oxadiazole isomer presented monotropic liquid crystalline properties on cooling with nematic mesomorphism in a narrow range. The mesomorphic properties are strongly dependent on the nature of the central core (oxadiazole isomers), and the results obtained may provide a better understanding of the nature of mesogens and their use in many industrial applications.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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