

Mesomorphic Properties of Heterocyclic 1,3-oxazepane-4,7-diones Compounds

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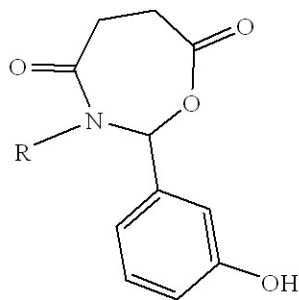
Abstract: The mesomorphic properties of a homologous series of 2-(3-hydroxyphenyl)-3-alkyl-1,3-oxazepane-4,7-diones, containing even number of carbon (2, 4, 6, 8, 10, 12, 14, 16 and 18) adjacent to the nitrogen atom of heterocyclic core, were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The result indicated that the oxazepane compounds are not mesogenic. Effects of the terminal alkyl group chain on the mesomorphic properties are discussed.

Key word: 1,3-oxazepane-4,7-diones; mesomorphic properties, Cr₁; Cr₂.

INTRODUCTION

In the field of liquid crystal synthesis, mesogenic compounds containing heterocyclic rings are increasingly found (Matharu and Asman 2007; Gallardo *et al.*, 2009). The incorporation of heterocyclic moieties as core units in thermotropic liquid crystals can result in large changes in their mesophases and physical properties due to which they possess more polarisable heteroatoms, such as nitrogen, oxygen and sulfur atoms (Seed 2007; Meyer *et al.*, 1998; Bartuli'n *et al.*, 1993). Seven-membered heterocyclic 1,3-oxazepane-4,7-diones is a type of a compound consisting of nitrogen and oxygen atoms with two carbonyl compounds. The oxazepine core has been widely investigated in biological activity (Crimmins and Choy 1999; Taunton *et al.*, 1996; Bong *et al.*, 2001; Jarvo and Miller 2002; Nagarajan *et al.*, 1985). Our interest in modification of oxazepine core as liquid-crystalline compounds has been reported in earlier publication (Yeap *et al.*, 2010)

For this study, the core of oxazepane based liquid crystal was investigated. The structure of compounds is shown in figure 1.



1-9

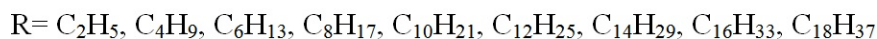


Fig. 1: The molecular structure of 2-(3-hydroxyphenyl)-3-alkyl-1,3-oxazepane-4,7-diones (1-9)

Experimental:

The experimental part for the synthesis of novel 2-(3-hydroxyphenyl)-3-alkyl-1,3-oxazepane-4,7-dione and recording of all NMR data have been describe elsewhere (Mohammad *et al.*, accepted; Mohammad *et al.*, 2011 in press).

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RESULTS AND DISCUSSION

The mesomorphic properties of the title compounds are investigated using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The sequence of phase and related transition temperatures, upon heating and cooling runs for compounds, are listed in Table 1. Figure 2 depicts the DSC thermograms of compound 6 during the heating and cooling scans. Phase identification was made by comparing the observed textures with those textures reported in the literatures (Demus and Richter 1978; Dierking 2003). The melting points are always equal to or higher than clearing points, hence exhibiting supercooling properties (Liu 1981).

It can be seen from Table 1 that the 1,3-oxazepanedions compounds are non-mesogenic compounds. The DSC thermograms for compounds 1-5 during heating cycle show, only one peak that can be ascribed to direct isotropization process (Cr-to-I). Under polarizing optical microscope study, crystal phase texture was observed which in turn changed to dark region isotropic, during heating run. A transition from crystal to isotropic for compounds 1-5 is observed on heating at 87.60 °C, 93.78 °C, 99.83 °C, 103.87 °C and 104.16 °C, respectively. On the reverse, a transition from isotropic to crystal is observed on cooling at 52.67 °C, 71.52 °C, 73.42 °C, 75.50 °C and 86.65 °C, respectively.

Table 1: Phase transition temperatures (°C) and the corresponding enthalpies (J/g) of compounds 1-9.

Compounds	Transition temperature °C Heating/ Cooling(corresponding enthalpy changes in KJmol ⁻¹)
1	Cr 87.60(40.18) I Cr 52.67(-26.69) I
2	Cr 93.78(62.54) I Cr 71.52(-49.31) I
3	Cr 99.83(60.50) I Cr 73.42(-44.19) I
4	Cr 103.87(49.90) I Cr 75.50(-51.19) I
5	Cr 104.16(37.17) I Cr 86.65(-24.78) I
6	Cr ₁ 84.51(13.21) Cr ₂ 95.30 (28.71) I Cr ₁ 75.20(-11.30) I
7	Cr ₁ 75.33(9.84) Cr ₂ 101.69 (66.42) I Cr ₁ 45.20(-32.11) Cr ₂ 72.57 (-60.41) I
8	Cr ₁ 89.42(29.79) Cr ₂ 119.66 (59.24) I Cr ₁ 52.16(-27.21) Cr ₂ 87.35 (-39.20) I
9	Cr ₁ 76.58(15.40) Cr ₂ 113.30 (23.10) I Cr ₁ 76.31(-11.20) Cr ₂ 89.31 (-40.12) I

In compound 6, it is noted that it does not form liquid crystal phase, and show only the phase sequence between the Cr₁-Cr₂-I on cooling at 84.51 °C, and 95.30 °C respectively. While, the phase transition between the isotropic liquid to crystal upon cooling is also observed at 75.20 °C.

Moreover, the compound 7, 8 and 9 were not mesogenic and showed only a phase sequence of Cr₁- Cr₂- I upon heating process at 75.33 °C, 101.69 °C, 89.42 °C, 119.66 °C, 76.58 °C and 113.30 °C, respectively. In addition, a phase sequence of I- Cr₂- Cr₁ is also observed upon cooling process for respective compound 7, 8 and 9 at 72.57 °C, 45.20 °C, 87.35 °C, 52.16 °C, 89.31 °C and 76.31 °C, respectively. Figure 3 shows the photomicrographs of textures on heating and cooling for compound 6.

In conclusion, the study of mesomorphic properties of heterocyclic 1,3-oxazepane-4,7-diones was investigated. The high values of the enthalpy of the phase transition determined from DSC prove the crystallization and Cr₁-Cr₂ modification. The phenomenon is not accompanied by textural changes in the optical microscope. In future work, the oxazepine core with ether and ester will be further investigated.

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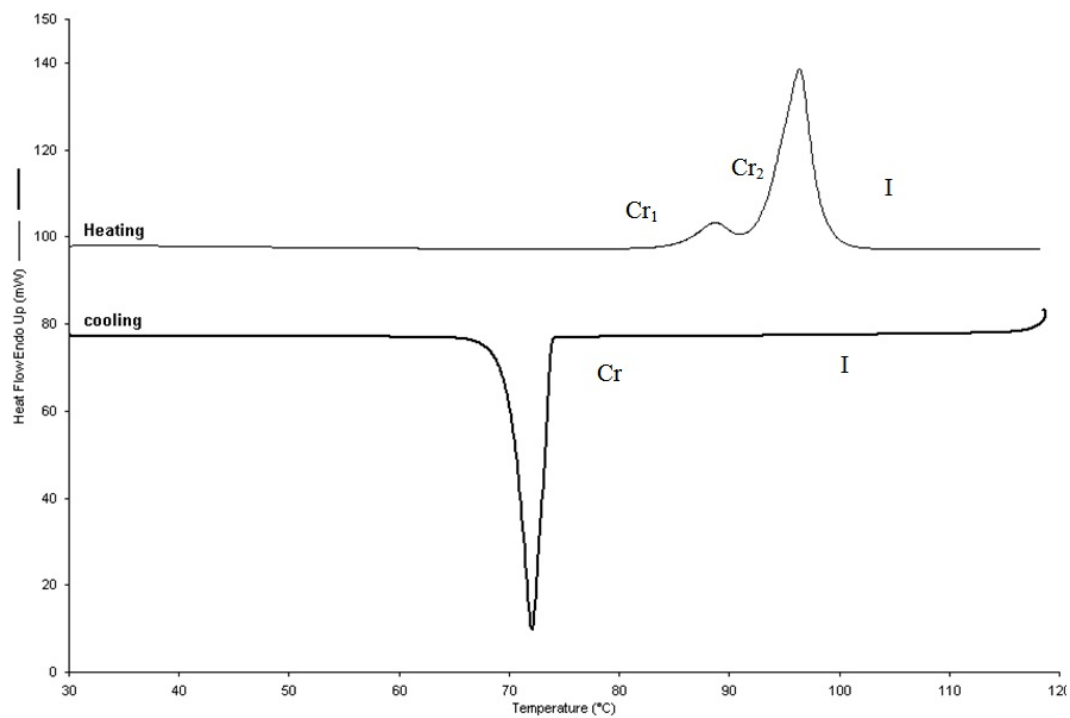


Fig. 2: DSC plot on heating and cooling for selected compound 6

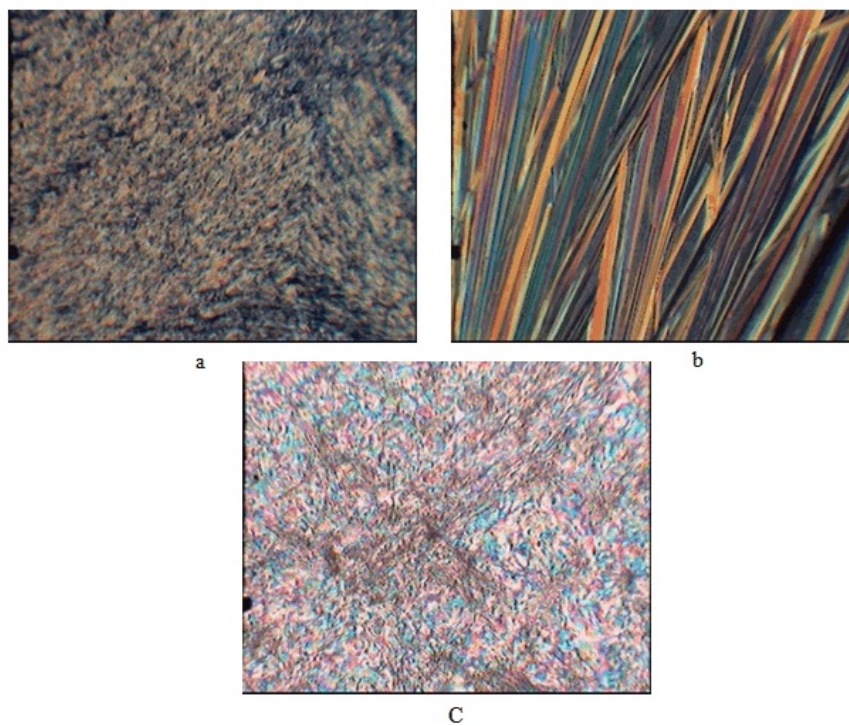


Fig. 3: Photomicrographs for compound 6(a) on heating Crystal phase (Cr₁) at 86.90 (b) on heating Crystal phase (Cr₂) at 97.33 (c) on cooling crystal phase Cr at 73.56 °C.

REFERENCES

- Bartuli'n, J., R. Martinez, H. Gallardo, H. Muller, T.R. Taylor, 1993. *Mol. Cryst. Liq. Cryst.*, 225, 175.
- Bong, T.D., T.D. Clark, J.R. Granja, M.R. Chadiri, 2001. *Angew. Chem. Int. Ed.*, 40- 988.
- Crimmins, M.T., A.L. Choy, 1999. *J. Am. Chem. Soc.*, 121, 5653.
- Demus, D., L. Richter, 1978. *Textures of Liquid Crystals*, verlag Chemie, New York.
- Dierking, I., 2003. *Textures of Liquid Crystals*, Wiley-VCH, Weinheim.
- Gallardo, H., F.R. Bryk, A.A. Vieira, T.E. Frizon, G. Conte, B.S. Souza, J. Eccher, I.H. Bechtold, 2009. *Liq. Cryst.*, 36: 839.
- Jarvo, E.R., S.J. Miller, 2002. *Tetrahedron*, 58: 2481.
- Liu, C.T., 1981. *Mol. Cryst. Liq. Cryst.*, 74, 25.
- Matharu, A.S., D.C. Asman, 2007. *Liq. Cryst.*, 34: 1317.
- Meyer, E., C. Zucco, H. Gallardo, 1998. *J. Mater. Chem.*, 8: 1351.
- Mohammad, A. T., H. Osman, G.Y. Yeap, (Accepted).
- Mohammad, A.T., H. Osman, G.Y. Yeap, 2001, *Int. J. Spect.* in press.
- Nagarajan, K., J. David, G. A. Bhat, 1985. *Ind. J. Chem. Sect. B.*, 24B: 840.
- Seed, A., 2007. *Chem. Soc. Rev.*, 36: 2046.
- Taunton, J., J.L. Collins, S.L. Schreiber, 1996. *J. Am. Chem. Soc.*, 118: 10412.
- Yeap, G.Y., A.T. Mohammad, H. Osman, 2010. *J. Mol. Struct.*, 982: 33.