

Synthesis and Mesomorphic Properties of Novel γ -Substituted β -Diketonates

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Abstract: The synthesis and mesomorphic properties of two series of novel γ -substituted β -diketonates have been reported. All of the compounds 2,4-dioxo-3-pentyl 4-[[4-(*n*-alkoxyl) cinnamoyl]oxy]cinnamatetes **Ia-If** (*n*=7-12) exhibit two monotropic phases (N and Sc) and have a wider mesophase range than the compounds 2,4-dioxo-3-pentyl 4-[[4-(*n*-alkoxyl) benzoyl]oxy] cinnamatetes **IIa-IIf** (*n*=7-12), which display one monotropic nematic phase (*n*=7-10) or an enantiotropic nematic phase for *n*=11 or two enantiotropic phases (N and Sc) for *n*=12.

Keywords: γ -Substituted β -diketonates, liquid crystal, synthesis.

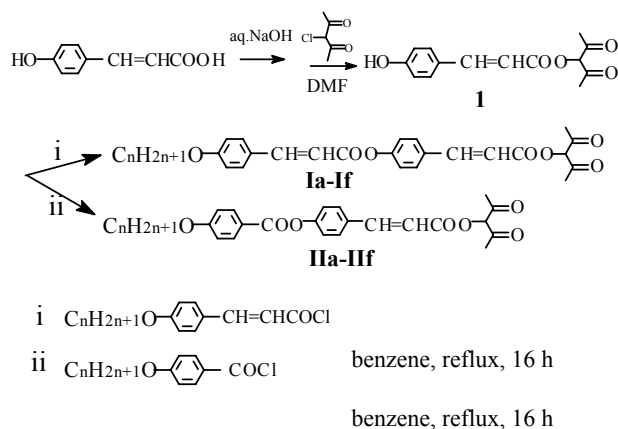
γ -Substituted β -diketonates are important precursors for the synthesis of mesogenic heterocycles or metallomesogenic derivatives. Mesogenic pyrazoles and isoxazoles obtained *via* β -diketonates have been reported previously in the literature¹⁻², and β -diketonates have been widely used as organic ligands in mesogenic coordination complexes of many transition metals³⁻⁴. Although a large number of β -diketonates has been reported to date, only a few examples of mesogenic β -diketonates have been published. We have reported a series of γ -substituted β -diketonates, but most of them are non-mesogens⁵⁻⁶. Two reasons may account for this result (i) the length-to-breadth of the molecules is not big enough to form calamitic mesogens and (ii) the conjugation of the molecules can not form enough mesogenic core, both of which are basic factors to the formation of the mesomorphic phases. In this paper, we report two series of new β -diketonates (**Scheme I**), all of which are mesogens. The effect of the structure of the molecules on the mesomorphism has also been discussed.

2,4-Dioxo-3-pentyl 4-hydroxyl cinnamate **1**⁷ was prepared by reaction of sodium *p*-hydroxycinnamate with 3-chloropentane-2,4-dione in anhydrous DMF. The compounds **Ia-If**⁸ and **IIa-IIf**⁹ are synthesized by condensation of the compound **1** with 4-(alkoxyl)cinnamoyl chloride and 4-(alkoxyl)benzoyl chloride, respectively, in good yields. The structures and the purities of the compounds **1**, **Ia-If** and **IIa-IIf** were ascertained by IR, MS, elemental analysis and ¹H-NMR spectroscopic data.

The transition temperatures and thermal behaviors were determined using a dif-

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Scheme I

**Table 1.** Transition temperatures ($^{\circ}C$) and transition enthalpies ($kJ\ mol^{-1}$) of **I**, **II**

n	I	II
a 7	Cr. 128.7 (34.31) Iso. Iso. 96.5 (-0.37) N. N. 84.2 (-0.32) Sc. Sc. 44.1 (-0.66) Cr.	Cr. 75.74 (37.92) Iso. Iso. 42.32 (-0.24) N. N. 37.62 (-0.36) Cr.
b 8	Cr. 129.8 (35.54) Iso. Iso. 97.0 (-0.43) N. N. 86.8 (-0.57) Sc. Sc. 45.3 (-2.15) Cr.	Cr. 77.8 (46.07) Iso. Iso. 46.9 (-0.34) N. N. 43.9 (-0.72) Cr.
c 9	Cr. 125.0 (38.47) Iso. Iso. 99.6 (-0.42) N. N. 91.2 (-0.36) Sc. Sc. 51.4 (-1.98) Cr.	Cr. 65.70 (38.73) Iso. Iso. 48.92 (-0.26) N. N. 46.17 (-0.77) Cr.
d 10	Cr. 126.8 (47.48) Iso. Iso. 106.8 (-0.53) N. N. 98.7 (-0.45) Sc. Sc. 68.9 (-4.12) Cr.	Cr. 66.52 (18.16) Iso. Iso. 52.39 (-0.37) N. N. 48.36 (-1.22) Cr.
e 11	Cr. 122.1 (43.48) Iso. Iso. 104.2 (-0.62) N. N. 98.7 (-0.49) Sc. Sc. 68.9 (-3.76) Cr.	Cr. 41.66 (25.67) N. N. 57.66 (4.46) Iso.
f 12	Cr. 125.7 (46.03) Iso. Iso. 106.4 (-2.86) N. N. 102.7 (-1.16) Sc. Sc. 46.1 (-3.55) Cr.	Cr. 48.39 (21.03) N. N. 58.41 (10.34) Sc. Sc. 64.51 (12.24) Iso.

Cr, crystals; N, nematic phase; Sc, smectic C phase; Iso, isotropic liquid;

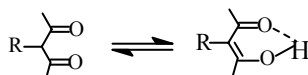
ferential scanning calorimeter and a polarizing microscope equipped with a hot stage. The mesophases had been identified according to the textures observed by optical microscopy¹⁰. The thermal behaviors of the β -diketonates **Ia-IIf** and **IIa-IIIf** are summarized in **Table 1**.

As shown in **Table 1**, the β -diketonates **I** and **II** had different liquid crystal behaviors. All of the compounds in series **I** exhibit two monotropic phases (N and Sc)

and have not only a wider mesophase range but also a higher transition temperature than series **II**. In contrast, the β -diketonates **IIa-IId** display one monotropic phase (N), while **IIe** has one enantiotropic phase (N) and **IIf** shows two enantiotropic phases (N and Sc). The different mesogenic properties between the β -diketonates **I** and **II** are due to

their different structures, the linking group between the two benzene ring of the former series (I) is a $-\text{CH}=\text{CHCOO}-$ group, while the latter is a $-\text{COO}-$ group. The $-\text{CH}=\text{CHCOO}-$ group is more beneficial than the $-\text{COO}-$ group to increase the molecular rigidity and planarity, which are advantageous to enhance the intermolecular interactions and the ordered arrangement of the molecules and form the mesomorphism. It is worthy to noting that the length of the alkoxy chain has a great effect on the mesogenic properties of the β -diketonates **II**. When the alkoxy chain becomes longer, the mesophases become more and the thermal stability of the mesophases increase from monotropic phase to enantiotrophase.

From the ^1H NMR data of the β -diketonates **I** and **II**, it is found that all the compounds exist in ketone and enol forms.



The proton in the enol form may increase the intermolecular interactions and promotes the ordered arrangement of the molecules by means of intermolecular H bonds. Both of the factors are beneficial to form the mesogenic phases. The presence of H bonds is a basic factor in the mesomorphism observed in these β -diketonates.

References and Notes

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7. Data for 2,4-Dioxo-3-pentyl 4-hydrocinnate **I**. Yield 76.4%; white powder; ^1H NMR (CDCl_3 , TMS) δ ppm: 14.45, 5.64 (2 \times s, 1H, CH), 7.70, 6.35 (2 \times d, 2H, J=16Hz, $-\text{CH}=\text{CH}-$), 7.40, 6.85 (2 \times d, 4H, J=8.0Hz, C_6H_4), 2.36, 2.05 (2 \times s, 6H, 2 \times CH_3); IR (KBr) v: 3366 (s,-OH), 1716 (s,ArC=O), 1631 (w, $-\text{CH}=\text{CH}-$), 1605, 1580, 1515 (s,Ar), 1266, 1204, 1149, 985 cm^{-1} ; MS (EI,70ev) m/z (%): 262 (M^+ ,2.52), 147(100); Elemental analysis for $\text{C}_{14}\text{H}_{14}\text{O}_5$: Calcd C, 64.12; H, 5.34; Found C, 63.88; H, 5.31.
8. Data for 2,4-dioxo-3-pentyl 4-[[4-(*n*-decyloxy) cinnamoyl]oxy] cinnate **Id**. Yield 82%; White powder; ^1H -NMR (CDCl_3 ,TMS) δ ppm: 14.50, 5.62 (2 \times s, 1H, CH), 7.80, 6.54 (2 \times d, 2H, J=16Hz, $-\text{CH}=\text{CH}-$), 7.72, 6.46 (2 \times d, 2H,J=16Hz, $-\text{CH}=\text{CH}-$), 7.62, 7.23 (2 \times d, 4H, J=8Hz, Ar), 7.52, 6.91 (2 \times d, 4H, J=8Hz, Ar), 3.99 (t, 2H, J=6Hz, RCH_2OAr), 2.34, 2.05 (2 \times s, 6H, 2 \times CH_3), 1.78 (m, 2H, CH_2), 1.24 (m, 14H, 7 \times CH_2), 0.87 (t, 3H, J=6Hz, CH_3); IR (KBr) v: 1722 (s, ArC=O), 1631(w, C=C), 1600, 1506 (s, Ar), 1287, 252, 1216, 1146 cm^{-1} (s,Ar-O-C); MS (EI,70ev) m/z (%): 548 (M^+ , 0.27), 287(100); Elemental analysis for $\text{C}_{33}\text{H}_{40}\text{O}_7$: Calcd C,72.26; H,7.30; Found C,72.31; H,7.42.
9. Data for 2,4-dioxo-3-pentyl 4-[[4-(*n*-decyloxy) benzoyl] oxy]cinnate **IId**. Yield 68.5%; White powder; ^1H NMR (CDCl_3 , TMS) δ ppm: 14.50, 5.66 (2 \times s, 1H, CH), 8.15, 7.30 (2 \times d, 4H, J=9Hz, Ar), 7.65, 6.99 (2 \times d, 4H, J=8.7Hz, Ar), 7.80, 6.58 (2 \times d, 2H, J=15.9Hz, $-\text{CH}=\text{CH}-$), 4.04 (t, 2H, J=6Hz, RCH_2OAr), 2.37, 2.08 (2 \times s, 6H, 2 \times CH_3), 1.85 (m, 2H, CH_2), 1.30 (m, 14H, 7 \times CH_2), 0.90 (t, 3H, J=6Hz, CH_3); IR (KBr) v: 1727 (s, ArC=O), 1635 (w, C=C), 1603,

1510 (s, Ar), 1258, 1211, 1164 cm^{-1} (s, Ar-O-C); MS (EI,70ev) m/z (%): 522(M^+ , 0.93), 121 (100); Elemental analysis for $\text{C}_{31}\text{H}_{38}\text{O}_7$: Calcd. C, 71.26; H, 7.28; Found C, 71.11; H, 7.38.

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Received 20 January, 2003