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Influence of bromoalkyloxy side chain on mesomorphic behavior in heterocyclic 7-(4-bromoalkyloxy)-3-(4'-decyloxyphenyl)-4*H*-1-benzopyran-4-ones

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Abstract

A new homologous series of isoflavone-based ethers, 7-(4-bromoalkyloxy)-3-(4'-decyloxyphenyl)-4H-1-benzopyran-4-ones were synthesized and characterized. The mesomorphic properties of all homologues were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Enantiotropic smectic A (SmA) phase was observed for all homologues. The structure–property study was carried out by comparing the mesomorphic behavior of the homologues with those previously reported analogues. The bromine atom from the alkyloxy side chain of the benzene ring fused to the heterocyclic moiety was found to be capable of changing the mesomorphic properties.

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Over the years, the classical calamitic isoflavone-based thermotropic liquid crystals consisting of a heterocyclic ring within the central core and one or two terminal chains have been studied and reported [1-3]. In order to study and understand the effect of different structural changes on the mesomorphism of these compounds, various modifications on existing molecules have been made keeping in view the molecular geometry of the isoflavone moiety [4,5]. The influence of different functional linkages, terminal chain length and polar terminal groups on the mesogenicity of liquid crystalline compounds has been reported [6-8]. Many hitherto reported works focused on the influence of polar lateral and terminal groups in the central moiety rather than in the terminal alkyloxy chain. Hence, we report herein the synthesis, characterization and effect of terminal bromine atom from the alkyloxy side chain (which is rare, at least to our knowledge) on the mesomorphic properties of newly derived isoflavone ethers, 7-(4-bromoalkyloxy)-3-(4'-decyloxyphenyl)-4H-1-benzopyran-4-ones 1–5. The synthetic routes toward the formation of all intermediates and title compounds are shown in Scheme 1 and their structures were elucidated by FT-IR and FT-NMR spectroscopic techniques [9].

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Scheme 1. Reactions and reagents. (a) KOH (2 equiv.), 1-bromodecane (1.2 equiv.), refluxing in methanol, 18 h; yield: 52%; (b) resorcinol (1.1 equiv.) in BF₃/Et₂O, N₂, 70–75 °C, 4 h; yield: 60%; (c) BF₃/Et₂O (4 equiv.) in DMF, N₂, 55 °C, 1 h; then in MeSO₂Cl (3 equiv.), N₂, 85 °C, 1.5 h; yield: 63%; (d) dibromoalkane, BrC_nH_{2n}Br (5 equiv.) (n = 4, 6, 8, 10, 12), K₂CO₃ (2 equiv.), refluxing in acetone, 6 h; yield: 70–78%.

Table 1 Phase transition temperatures and enthalpy change for compounds 1–5 upon heating and cooling.

| Compound | Phase transition, $^{\circ}$ C (enthalpy change, kJ mol ⁻¹) |
|---------------------------|---|
| 1 (<i>n</i> = 4) | Cr 105.3 (33.5) Cr ₂ 118.3 (29.0) SmA 169.7 (11.0) I |
| | I 167.0 (10.8) SmA 108.2 (30.6) Cr ₂ 98.4 (33.6) Cr |
| 2 (<i>n</i> = 6) | Cr 101.9 (55.0) SmA 152.8 (8.4) I |
| | I 149.3 (8.8) SmA 80.4 (52.5) Cr |
| 3 (<i>n</i> = 8) | Cr 108.0 (42.9) SmA 140.9 (10.5) I |
| | I 137.5 (8.8) SmA 79.7 (46.2) |
| 4 (<i>n</i> = 10) | Cr 111.6 (49.9) SmA 131.4 (10.4) I |
| | I 128.1 (9.9) SmA 91.7 (51.8) Cr |
| 5 (<i>n</i> = 12) | Cr 102.9 (7.4) Cr ₂ 111.8 (44.3) SmA 125.8 (8.0) I |
| | I 122.9 (7.6) SmA 85.0 (49.2) Cr |

Cr, crystal; SmA, smectic A; I, isotropic.

The phase transition temperatures and associated enthalpy changes of compounds 1-5 were measured by differential scanning calorimetry (DSC). The results obtained were listed in Table 1. The mesomorphic textures were determined by employing the polarizing optical microscope equipped with a hot stage and temperature controller. Phase identification was made by comparing the textures observed with those reported in the literature [10,11]. Observation under crossed polarizers showed that regardless of the brominated alkyloxy chain length, all homologues exhibited enantiotropic SmA phase which can be characterized by the formation of batonnets that coalesce to form focal conic fan-shaped textures. This suggests that the molecules are arranged in orthogonal layers. A typical morphology of these compounds can be shown by compound 2 in Fig. 1.

The mesomorphic behavior exhibited by this system was compared to those of the reported homologous series I [4] and II [5] in order to understand the structure–property relationships of these compounds. All homologues of this series and those of series I and II have a heterocyclic isoflavone moiety in the central core. The difference of structures between this series and series I can be ascribed to the presence of brominated alkyloxy chain in *n*-alkyloxy chain attached to the benzene ring fused with the heterocyclic moiety (ring A) whilst the present series differs from series II in term of the geometry of the terminal chain attached to the free benzene ring (ring B) (Fig. 2). Nematic (N) and smectic C (SmC) phases were observed in addition to SmA phase in series I. The introduction of a Br atom in place of H atom (present series) or a branched methyl group (series II) in the flexible terminal chain gives rise to a change in the mesomorphic behavior as compared to series I. Homologues in the present series exhibit monomorphic SmA phase independent of chain length. Since the mesomorphic properties of a compound are a consequence of the balance between the attractive (due to polarizability and polarity) and repulsive forces (governed by steric effect), the presence of a polar and polarizable

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Fig. 1. Focal conic fans of SmA phase exhibited by compound 2.



Fig. 2. Comparison between the molecular structures of compounds 1-5 and their analogues.

Br atom facilitates lamellar packing (due to polarizability and polarity) of molecules leading to the formation of SmA. However, this phenomenon also prevents and spatially destabilizes the tilted arrangement of molecules (due to steric effect when molecules are tilted) which could lead to the formation of SmC phase. A reduced compatibility of geometry when the terminal chain is branched (series **II**) may disrupt the tilted arrangement that is essential for the formation of SmC phase. The average smectic thermal stability of the present series is similar to that of series I. Large mesomorphic ranges (>30 °C) and high clearing temperatures (>120 °C) were recorded for compounds in both series. However, the average mesomorphic range of series II (<10 °C) is much narrower than the two formerly mentioned series which can be rationalized in term of a reduced surface area for intermolecular van der Waals interactions when one of the terminal chains is branched which results in a decreased stability of the mesophase [5].

A graphical presentation of the clearing temperatures as a function of the number of carbon atoms in the brominated alkyloxy terminal chain for the present series is shown in Fig. 3. There is a gradual decrease in clearing temperatures as the length of the brominated alkyloxy side chain increases in which the homologue having the longest side chain possesses lowest thermal stability. This phenomenon can be explained in term of dilution effect of the flexible chains as reported for a series of laterally branched azobenzenes [13]. This observation is also in good agreement with the previously reported homologous series, N,N'-bis(3-methoxy-4-alkoxybenzylidene)-1,4-phenylenediamines [14]. It suggests that the flexibility of the long terminal chain prevents the long molecular axis from remaining in a fully stretched geometry but tends to coil resulting in the non-linearity of the molecule when the terminal chain length increases [12]. Furthermore, this could probably be due to the repulsive (steric) forces leading to larger intermolecular distance. This can be considered as a consequence of deviation from linearity of the terminal alkyloxy chains with increasing length.



Fig. 3. Plot of clearing temperatures of compounds 1-5 as a function of the number of carbon atoms.

In conclusion, all homologues of this series exhibit stable, enantiotropic liquid crystalline smectic A phase which was found to be independent of side chain. The stability of the mesophase is attributable to the polar Br atom at the end of the alkyloxy chain together with the planarity and enhanced polarity of the oxygen atoms of the ether linkages as well as the heterocyclic central moiety.

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- [9] Analytical and spectroscopic data for representative compound 3: Yield 72%, anal: calcd. for $C_{33}H_{45}BrO_4$, C 67.68, H 7.75, found, C 67.58, H 7.76%. IR (max (KBr, cm(1): 2920, 2853 (C–H aliphatic), 1635 (C=O), 1609 (C=C), 1251 (C–O), ¹H NMR (CDCl₃): δ 8.23 (d, 1H, *J* = 8.7, Ar-H), 7.93 (s, 1H, Ar-H), 7.51 (d, 2H, *J* = 8.8, Ar-H), 7.01–6.97 (dd, 3H, *J* = 8.7, *J* = 2.1, Ar-H), 6.86 (d, 1H, *J* = 8.7, Ar-H), 4.07 (t, 2H, OCH₂), 4.01 (t, 2H, OCH₂), 3.44 (t, 2H, BrCH₂), 1.93–1.86 (m, 2H, BrCH₂CH₂), 1.84–1.78 (m, 2H, OCH₂CH₂), 1.54–1.42 (m, 2H, OCH₂CH₂), 1.41–1.30 (m, 22H, Alkyl-H), 0.90 (t, 3H, CH₃). ¹³C NMR (CDCl₃): δ 176.25, 163.87, 159.56, 158.34, 152.37, 130.46, 128.11, 125.28, 124.43, 118.69, 115.21, 114.94, 100.97 (C_{arom}), 69.01, 68.49 (OCH₂), 34.28 (BrCH₂), 23.08–33.15 (CH₂), 14.51 (CH₃).
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