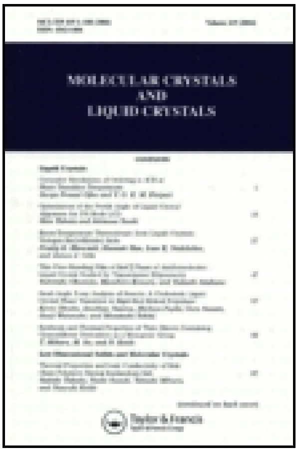

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

New Heterocyclic Mesogens with Benzopyran-2 H-One Moiety

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Version of record first published: 04 Oct 2006.

To cite this article: N. K. Chudgar & S. N. Shah (1991): New Heterocyclic Mesogens with Benzopyran-2 H-One Moiety, Molecular Crystals and Liquid Crystals, 204:1, 65-70

To link to this article: http://dx.doi.org/10.1080/00268949108046594

Mol. Cryst. Liq. Cryst., 1991, Vol. 204, pp. 65–70
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Printed in the United States of America

New Heterocyclic Mesogens with Benzopyran-2 H-One Moiety

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(Received July 26, 1990)

Mesogen with benzopyran-2 H-one moiety are rare. However, Trivedi *et al.* have reported mesogenic benzopyran-2 H-one. Recently, Vora *et al.* have reported mesogenic polymers with benzopyran-2 H-one moiety and evaluated its fluorescent behaviour. In view of the rarity of mesogens with benzopyran-2 H-one moiety and their potential as fluorescent compounds, homologous series of 3-Bromo-4-Methyl-2-oxo-2 H-1-benzopyran-7-yl-4′-*n*-alkoxy benzoates was synthesized and the mesomorphic behaviour has been studied. Lower members are non-mesogenic where as higher members of the series exhibit monotropic smectic phase. Transition temperatures are also identified using DSC. The thermal stabilities of present series is compared with the corresponding homologous series of benzopyran-2 H-one derivatives. All the synthesized compounds are characterized by elemental analysis and spectroscopic studies.

Keywords: LC synthesis, heterocyclic, benzopyran

INTRODUCTION

Mesogens with oxygen heterocyclic moiety are relatively less studied.[1–5] However, Trivedi[6,7] *et al.* Nakai *et al.*[8] and Anisimova *et al.*[9] have reported mesogenic benzopyran 2-H-one. Vora *et al.*[10] have reported mesogenic polymers with benzopyran 2 H-one moiety and evaluated its fluorescent behaviour. Recently, Tadashiro *et al.*[11] reported 3-cyano-2-oxo-2H-1-benzopyran-7-yl-4′-*n*-alkoxy benzoates and 2-phenyl-4-oxo-4H-1-benzopyran-6-yl-4′-*n*-alkoxy benzoates as mesogenic compounds. In view of the rarity of mesogens with benzopyran-2 H-one moiety and their potential as fluorescent compounds homologous series 3-bromo-4-methyl-2-oxo-2H-1-benzopyran-7-yl-4′-*n*-alkoxy benzoates (Series-I) was synthesized and the mesogenic properties have been studied.

EXPERIMENTAL

Microanalysis of compounds were performed on Coleman instrument. UV spectra were recorded on Shimadzu UV VIS 240. IR spectra were recorded on Shimadzu IR-408. NMR spectrum was recorded on Perkin-Elmer R-32. Liquid crystalline properties were investigated on Leitz Labourlux polarizing microscope provided with heating stage. DSC were investigated on the Perkin-Elmer DSC-4.

7-Hydroxy-4-methyl-2-oxo-2H-1-benzopyran and its 3-bromo derivative were prepared by known methods[12,13] 4-*n*-alkoxy benzoic acids, their acid chlorides and the esters of 7-hydroxy-4-methyl-3-bromo-2-oxo-2H-1-benzopyran were synthesized as per the known methods.[14]

Elemental analysis of all the compounds were found to be satisfactory.

Spectral analysis of the 3-bromo-4-methyl-2-oxo-2 H-1-benzopyran-7-yl-4′-*n*-alkoxy benzoates: U.V. ($CHCl_3$): λ_{max} 280, 312 nm

I.R. (KBr): ν 2900–2825 (C—H stretching), 1740 (—COO—), 1720 (benzopyran ketone), 1600 and 1505 (aromatic), 1480 (alkyl chain —CH_2—), 1420 (—CH_3), 1040 (—C—O—) 690–680 and 660 (C—Br) cm^{-1}

NMR (90 MHz, $CDCl_3$) of compound No. 4 in the Table I, δ, 8.15 (*d*, $J = 9$ Hz, 2H, proton at, C_2', and C_6'), 7.7 (*d*, $J = 9$ Hz, 1H, proton at C_6), 7.35–7.20 (*m*, 2H, proton at C_5 and C_8), 6.95 (*d*, $J = 9$ Hz, proton at C_3' and C_5'), 4.1 (*t*, 2H, —O—CH_2), 2.65 (*m*, 3H, —CH_3 group at C_4), 2.05–1.35 (*m*, 4H, —CH_2—CH_2— of butoxy-chain), 1.15–0.6 (*m*, 3H, terminal CH_3 of butoxy chain).

Mass spectrum was recorded for compound No. **8** Table I *m*/*e*: 488 (M + 1), 460, 408, 375, 345, 308, 269, 233 (base peak), 205, 175, 161, 147, 121, 93, 65.

TABLE I

Melting points and transition temperatures of 3-bromo-4-methyl-2-oxo-2 H-1-benzopyran-7-yl-4′-*n*-alkoxy benzoates

Compound No.	Alkyl group	Transition temperatures °C Smectic	 Isotropic liquid
1	Methyl	—	237.0
2	Ethyl	—	212.0
3	Propyl	—	179.0
4	Butyl	—	167.0
5	Pentyl	—	145.0 142.2*
6	Hexyl	—	147.0
7	Heptyl	—	132.0
8	Octyl	—	137.0
9	Nonyl	(98.0) (97.6)*	124.0 119.0*
10	Decyl	(104.0)	125.0
11	Dodecyl	(111.0) (112.0)*	130.0 127.6*
12	Tetradecyl	(118.0) (114.6)*	130.0 127.0*
13	Hexadecyl	(119.0) (115.5)*	128.0 126.2*
14	Octadecyl	(103.0)	107.0

Values in parenthesis indicate monotropy.

* Indicate Transition Temperature identified by D.S.C.

RESULTS AND DISCUSSION

Melting points and transition temperatures of the compounds of the present series are compiled in Table I.

The first eight homologues of the present series are non-mesomorphic, mesomorphism appear at the nonyl derivatives which is monotropic smectic and remains monotropic up to the last homologue studied. On cooling the isotropic liquid, batonnets separate from it and coalesce together to form fan shaped focal-conic texture in each case. The smectic phase observed in present study is smectic A type. Thakar *et al.*[15] and Nakai *et al.*[8] have explained the smectogenic tendencies of benzopyran-2-one derivatives on the ground that benzopyran-2-one nucleus favours smectic phase formation, due to presence of asymmetric and large dipole moment in benzopyran-2-one skeleton. Present study further confirms the above observation of Thakar *et al.* and Nakai *et al.*

Figure 1 shows the relationship of transition temperatures to carbon numbers in the alkoxy chain. The smectic-isotropic transition temperature curve rises in a smooth fashion, it reaches to maxima and then falls off.

During the synthesis of present series-I, few members of the 4-methyl-2-oxo-2 H-1-benzopyran-7-yl-4′-*n*-alkoxy benzoates (where R = C_7H_{15} and $C_{14}H_{29}$) were synthesized. Both the compounds were found to be non-mesogenic. However, the introduction of the Bromine atom at 3-position of benzopyran induces mesogenic properties from the nonyl members onwards. Thus increase in polarizability at 3-position enhances the mesogenic properties.

The dipole moment of about 4.9 D from the benzopyran-2-one skeleton is preferably in perpendicular to long molecular axis,[8] bulky bromine group and methyl group present at the 3 and 4 position of benzopyran-2-one respectively may be responsible for the non-mesogenic nature of the first eight members of the present series. However, nonyloxy onwards all members of the present series show monotropic smectic-A phase. This may be attributed to the flexible ester central linkages, long chain alkoxy substituent, one phenyl and one benzopyran system.

The average thermal stabilities (Table II) of the present Series-I is compared with corresponding homologous series of benzopyran-2 H-one derivatives (Figure 2).

The average thermal stabilities of present Series I and Series A is almost same. The geometry of Series I and A is almost same except the terminal groups present at the 3 and 4 positions of the benzopyran-2-one moiety. In Series-I at 3-position is bromo group while in Series A it is benzoyl group at the same position. However, in Series I laterally substituted methyl group is present at 4-position of benzopyran-2-one where as in Series A there is no substituent at that position.

These geometrical differences result into the changes in polarizability and acoplanarity of both the systems. However, net effect of these forces are almost same as evidenced from equal smectic thermal stabilities of both the series. In both the series mesophases commence late but effect is more severe in Series A. This can be attributed to benzoyl group present at 3-position of benzopyran-2-one moiety.

Geometry of Series I, series B and Series C differ in substituents at 3 and 4-position. In Series I at 3-position is bromo group and methyl group at position-4

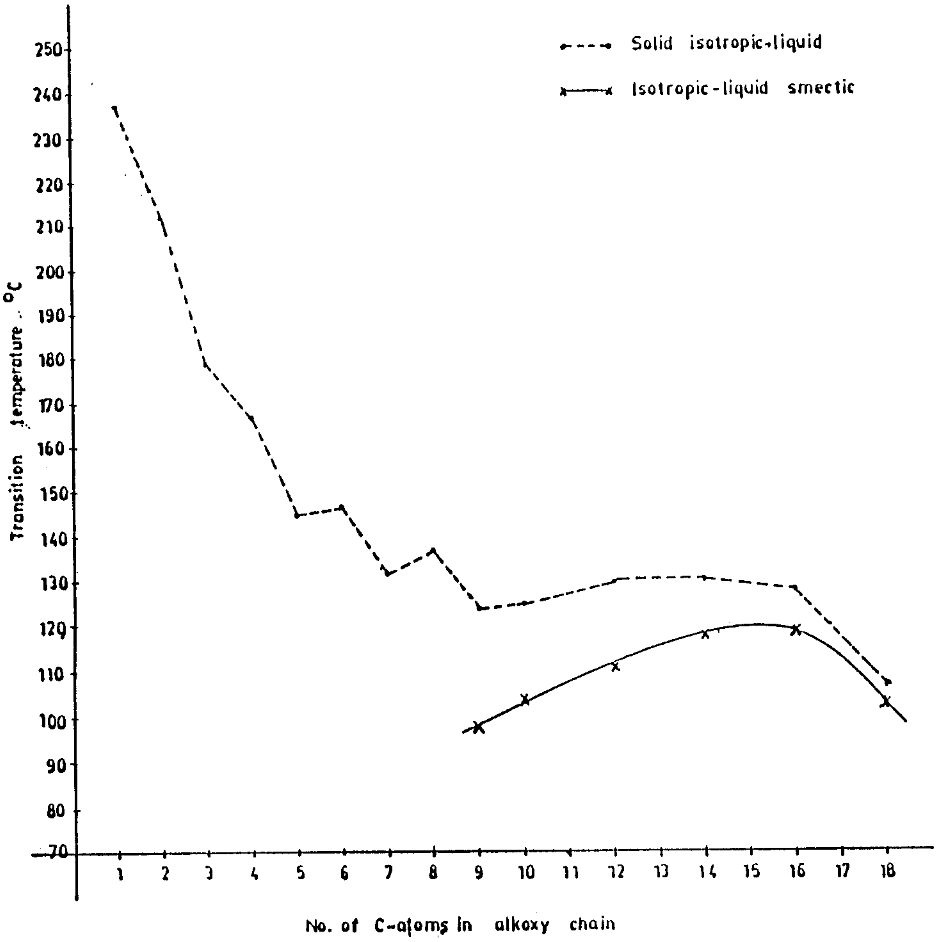

FIGURE 1

TABLE II

Average thermal stabilities

	I	A[15]	B[6]	C[7]
Smectic-Isotropic or Isotropic-Smectic C_{12}, C_{14}, C_{16}, C_{18}	112.75	112.62	124.62	158.75
Commencement of smectic phase	C_9	C_{12}	C_6	C_5

while carboxy ethyl and acetyl groups are present at 3-position of benzopyran-2-one in the Series B and Series C, respectively. The polarizability will increase due to the introduction of carboxy ethyl and acetyl group at 3-position of the benzopyran in Series B and C, respectively, which is responsible for the higher thermal stabilities of Series B and C. In Series I introduction of bromine atom increases the polar-

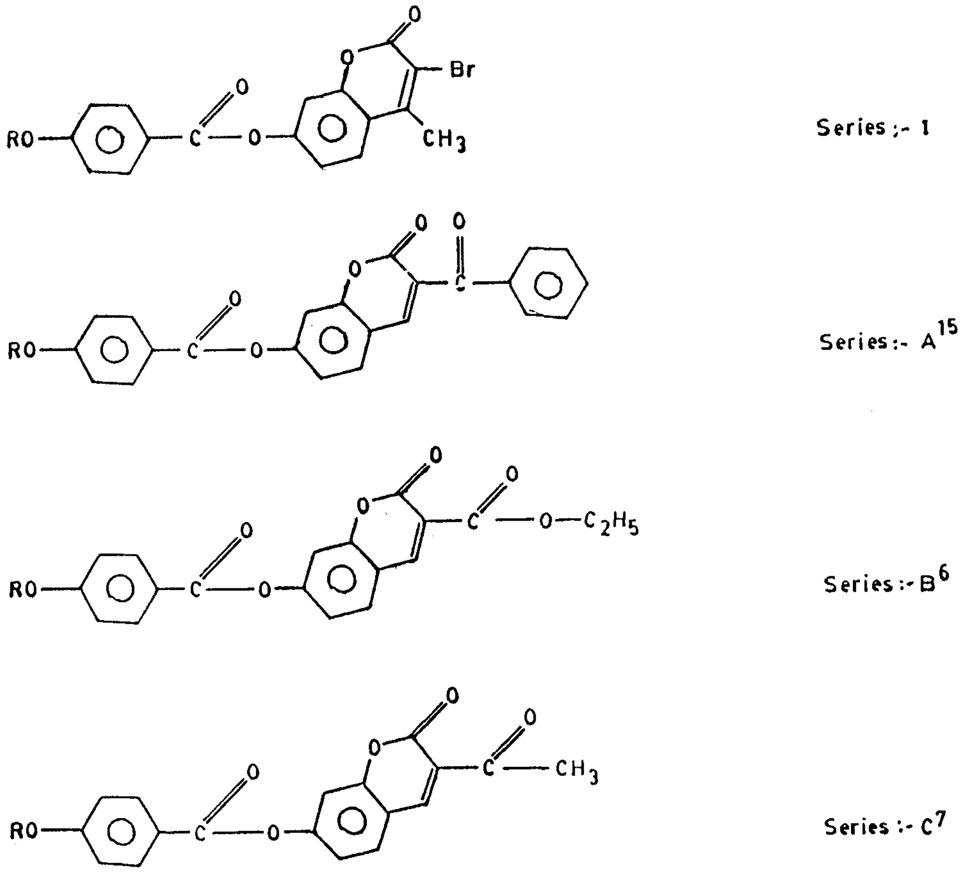

FIGURE 2

izability but at the same time presence of laterally substituted methyl group at the 4-position of benzopyran ring system of present series reduces ideal geometry for mesophase formation, making present series thermally less stable compared to series B and C.

In conclusion, introduction of polarizable group at 3-position of 7-substituted benzopyran-2-one moiety induces mesogenic properties, but at the same time lateral substitution at 4-position of 7-substituted benzopyran-2-one moiety reduces mesogenic properties markedly.

Acknowledgments

We extend our deep sense of gratitude to Prof. P. K. Bhattacharya, Head, Chemistry Department for taking interest in our work and providing necessary facilities. Our sincere thanks are also due to Prof. R. A. Vora, Head, Applied Chemistry Department for his keen interest, constructive suggestions and fruitful discussions. We thank Shri S. S. Madhava Rao, Mrs. Sushila Amin, Petrofils Ltd. and Malti-Chem Centre for different analysis.

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