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Synthesis and characterization of 3-phenyl-4[H]-4-[one]-benzopyran (isoflavone) derivatives as potential mesogens

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With few mesogenic chromone derivatives in the literature the synthesis of 7-(4′-*n*-alkyloxybenzoyloxy) isoflavones was carried out. The resulting homologous series was characterized by elemental analysis and spectroscopic techniques. The first four members of the series only exhibit a nematic phase. In addition to the nematic phase, the smectic phase commences from the pentyloxy derivative. The decyloxy and higher derivatives only exhibit a smectic phase. The smectic phase observed in the present series is the smectic A type. Differential scanning calorimetry studies served the dual purpose of confirming the microscopic transition temperatures, as well as the calculation of the enthalpies of the various phase transitions.

Dioxolan derivatives have been studied extensively owing to their wide applicability in nematic electro optical display devices [1]. However, mesogenic mono-oxygen heterocycles [2–12] have been less exploited. In the recent past, Vora *et al.* [13] have reported mesogenic polymers containing a coumarin moiety. Not long ago Chudgar and Shah [14] studied mesogens with a central chalcone linkage, which may serve as precursers to flavones, flavanones, isoflavones and flavanols [15].

Isoflavones are the derivatives of 3-phenyl-4[H]-4-[one]-benzopyran. Basically a chromone derivative, these isoflavones comprise a varied class of natural products. To the best of our knowledge, isoflavone derivatives exhibiting mesogenic properties are as yet unknown. In this context, it was thought of interest to synthesize a homologous series of 7-(4′-*n*-alkyloxybenzoyloxy) isoflavones (ABI) and investigate the effect of the position of the keto group on mesogenicity.

The synthetic pathway for ABI is illustrated in figure 1. 7-Hydroxy isoflavones [16–18] and 4-*n*-alkyloxybenzoyl chloride [19] were synthesized by reported methods. The preparation of the 7-(4′-*n*-alkyloxybenzoyloxy) isoflavones (ABI) was carried out as follows. 7-Hydroxyisoflavone (0·02 mol) was dissolved in dry pyridine (5 ml) and a separately prepared cold solution of 4-*n*-alkyloxybenzoyl chloride (0·02 mol) in 5 ml of dry pyridine was added slowly to it, with constant stirring in an ice-bath. The mixture was allowed to stand overnight at room temperature. It was acidified with 1 : 1 dilute hydrochloric acid and the precipitates were washed with a cold, dilute solution of potassium hydroxide, followed by cold water. The esters were recrystallized repeatedly with a mixture of ethanol and acetic acid. The final recrystallization was done in ethyl acetate. The transition temperatures are recorded in the table.

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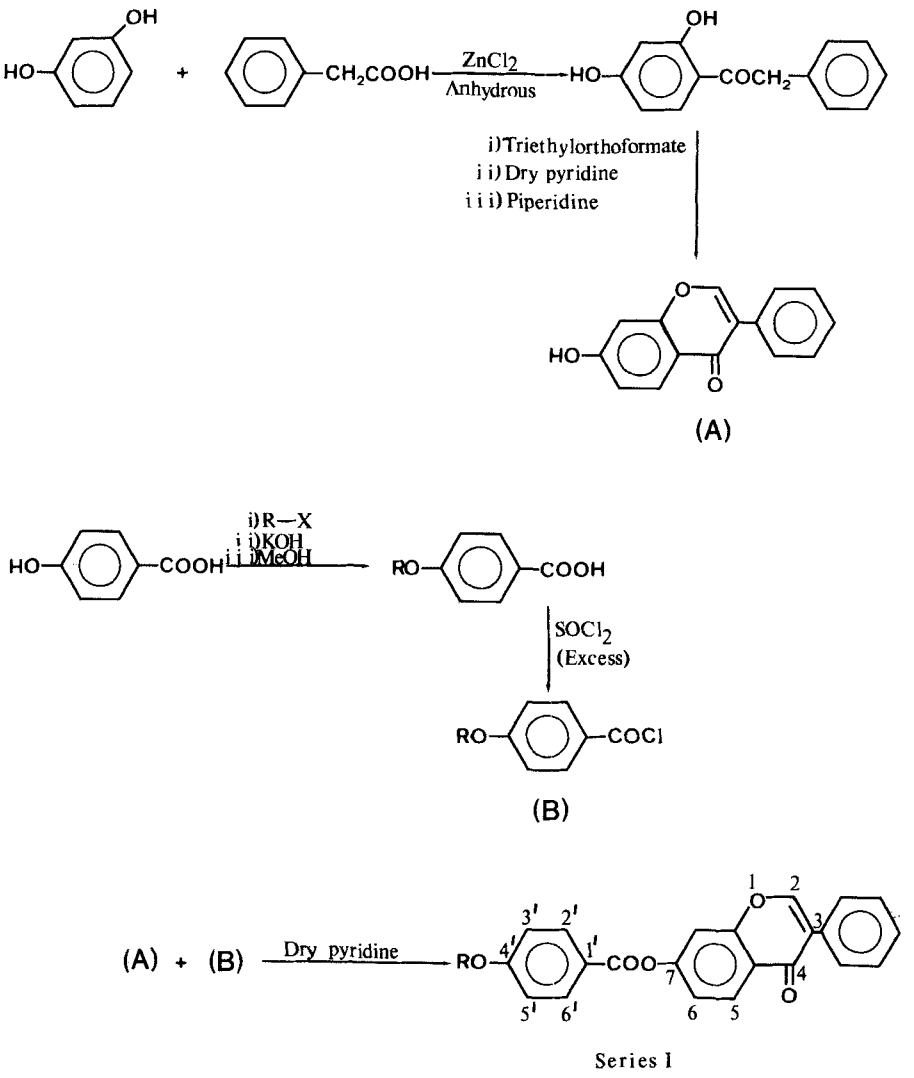

Series I

Figure 1. Synthetic route to series I.

Elemental analysis of all compounds agrees excellently with calculated values.

Spectral analysis of ABI: UV ($CHCl_3$): λ_{max} 262 nm, 305 nm. IR (KBr): ν 2925, 1740, 1640, 1605, 1445, 1040 cm^{-1}. NMR (90 MHz, $CDCl_3$) of compound **6**: δ 0·9 (m, 3 H, terminal $-CH_3$ of hexyloxy chain); 1·1–2·1 (m, 10 H, $(CH_2)_5$ of hexyloxy chain), 4·1 (t, 2 H, protons of $-OCH_2$ of hexyloxy chain), 7·0 (d, 2 H, $J = 9$ Hz, one proton at $C_{3'}$ and $C_{5'}$, respectively); 7·25–7·7 (m, 7 H, five protons of phenyl ring at C_3 and two protons at C_6 and C_8, respectively); 8·0 (s, 1 H, proton at C_2); 8·15 (d, 1 H, $J = 9$ Hz, C_5 proton); 8·35 (d, 2 H, $J = 9$ Hz, one proton at $C_{2'}$ and $C_{6'}$, respectively). NMR (90 MHz, $CDCl_3$) of compound **10**: δ 0·7–1·05 (m, 3 H, terminal CH_3 of decyloxy chain); 1·15–2·05 (m, 18 H, $(CH_2)_9$ of decyloxy chain); 4·1 (t, 2 H, protons of $-OCH_2$ of decyloxy chain); 7·0 (d, 2 H, $J = 9$ Hz, one proton at $C_{3'}$ and $C_{5'}$, respectively); 7·25–7·8 (m, 7 H, five protons of phenyl ring at C_3 and one proton at C_6 and C_8, respectively); 8·05 (s, 1 H, proton at C_2); 8·2 (d, 1 H, $J = 9$ Hz, proton at C_5); 8·45 (d, 2 H, $J = 9$ Hz, one proton at

Transition temperatures, DSC data and transition enthalpies for 7-(4′-*n*-alkyloxybenzoyloxy) isoflavones.

Compound	Alkyl group	Transition	Transition temperatures/°C		ΔH/kJ mol^{-1}
			Microscopic	DSC	
1	Methyl	C–N	184·0	186·1	13·23
		N–I	230·0	225·8	0·19
2	Ethyl	C–N	198·0	195·0	28·26
		N–I	234·0	230·3	0·72
3	Propyl	C–N	194·0	194·6	26·89
		N–I	214·0	213·2	0·62
4	Butyl	C–N	180·0	179·5	34·15
		N–I	217·0	213·5	0·43
5	Pentyl	C–S	170·0	171·8	33·14
		S–N	177·0	177·3	1·36
		N–I	205·0	204·6	0·44
6	Hexyl	C–S	162·0	159·7	21·98
		S–N	184·0	182·1	1·82
		N–I	206·0	204·6	0·15
7	Heptyl	C–S	159·0	161·6	33·71
		S–N	187·0	187·6	1·67
		N–I	196·0	199·7	0·49
8	Octyl	C–S	149·0	147·9	29·10
		S–N	191·0	191·3	1·71
		N–I	199·0	199·1	1·14
9	Nonyl	C–S	153·0	150·3	26·55
		S–N	195·0	194·2	1·99
		N–I	197·0	195·5	0·29
10	Decyl	C–S	139·0	139·9	8·03
		S–I	194·0	196·4	3·42
11	Dodecyl	C–S	147·0	142·0	30·78
		S–I	199·0	195·3	5·93
12	Tetradecyl	C–S	136·0	134·1	29·82
		S–I	196·0	193·4	4·75
13	Hexadecyl	C–S	130·0	133·4	61·53
		S–I	192·0	191·1	8·20
14	Octadecyl	C–S	125·0	124·6	46·23
		S–I	186·0	188·0	5·46

C: crystal; N: nematic; S: smectic A; I: isotropic liquid.

$C_{2'}$ and $C_{6'}$, respectively). The mass spectrum was recorded for the compound **2**. *m/e*: 386, 357, 341, 329, 317, 301, 273, 261, 237, 209, 192, 181, 163, 149 (base peak), 121, 109, 93, 76, 65, 51.

DSC studies were carried out with a view to confirm the observations under the microscope and to calculate the enthalpies of the phase transitions, (see the table).

The first four members of the series exhibit a nematic phase. The smectic phase commences from the fifth member (the pentyloxy derivative) which shows both smectic and nematic phases. From the tenth member onwards, the compounds display only the smectic mesophase. This phase is of a smectic A type, which is characterized by the formation of fan shaped focal conic textures on cooling (see figure 2).

The plot of transition temperatures against the number of carbon atoms in the alkyloxy chain (see figure 3) shows the usual odd–even effect for the nematic–isotropic transition temperatures. The curves for the nematic–isotropic and smectic–isotropic

Figure 2. Optical texture of smectic A phase observed with a polarizing microscope (× 140) at 171°C for 7-(4′-*n*-tetradecyloxybenzoyloxy) isoflavone.

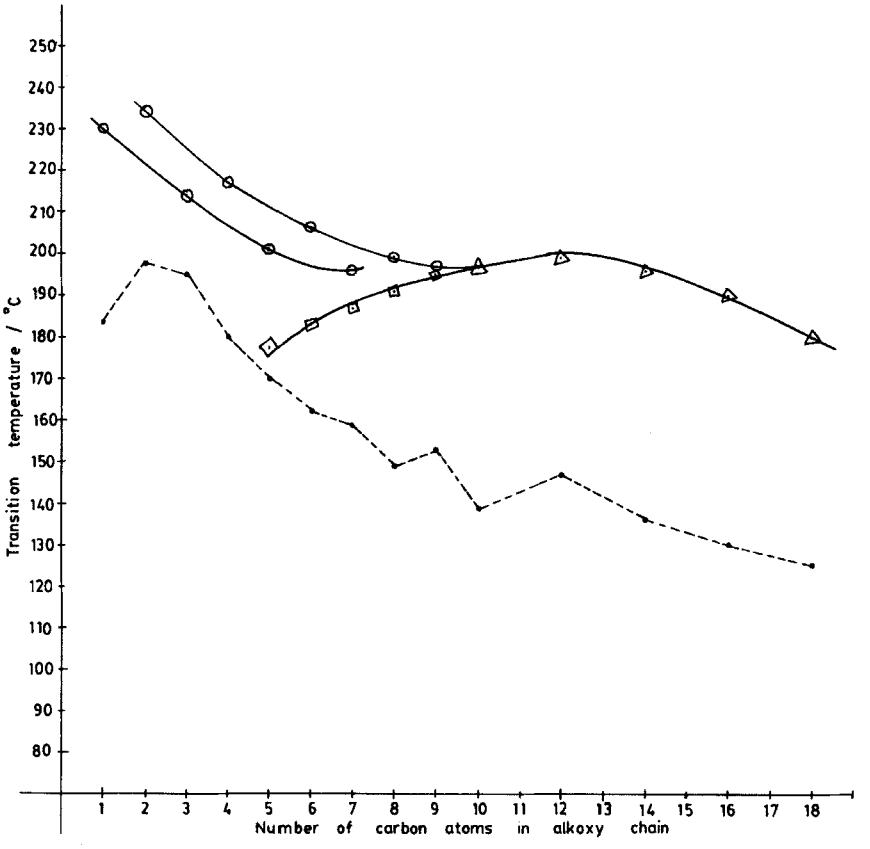

Figure 3. Graph of transition temperature versus number of carbon atoms in alkyloxy chain. ●---● Solid–mesomorphic; ⊙——⊙ nematic–isotropic; ⊡——⊡ smectic–nematic; △——△ smectic–isotropic.

transitions merge with each other and ultimately tend to rise as the chain length increases and levels off from higher members after exhibiting the maxima.

The present series exhibits mesomorphism of higher thermal stabilities as compared to series of other comparable flavone and coumarin derivatives [12, 20].

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References

[1] DEMUS, D., and ZASCHKE, H., 1981, *Molec. Crystals liq. Crystals*, **63**, 129.
[2] CHUDGAR, N. K., SHAH, S. N., and VORA, R. A., 1989, *Molec. Crystals liq. Crystals*, **172**, 51.
[3] CHUDGAR, N. K., and SHAH, S. N. (unpublished results).
[4] PAVLUCHENKO, A. I., SMIRNOVA, N. I., TITOV, V. V., KOVSHEV, E. L., and DJUMAEV, K. M., 1976, *Molec. Crystals liq. Crystals*, **37**, 35.
[5] VORA, R. A., GUPTA RENU, and PATEL, N. C., 1985, *Indian J. Chem.* B, **24**, 325.
[6] KELKAR, H., and SCHEURLE, B., 1969, *J. Phys., Paris, Colloque*, **4**, 104.
[7] CHUDGAR, N. K., and SHAH, S. N., 1990, *International Liquid Crystals Conference*, 22–27 July, Vancouver, Canada.
[8] ANISIMOVA, T. N., BOLOTIN, B. M., KIZEL, V. A., MADTI, V. A., and SKLYARUK, V. A., 1986, *J. appl. Spectrosc.*, **43**, 842.
[9] NAKAI, H., TAKENAKA, S., and KUSABAYASHI, S., 1983, *Bull. chem. Soc. Jap.*, **56**, 3571.
[10] THAKER, N. N., and TRIVEDI, K. N., 1981, *Indian J. Chem.* A, **20**, 566.
[11] NGUYEN, D. T., and PHAM, T. C., 1976, *Tap Chi Hoa Hoc*, **14** (4), 13.
[12] TADASHIRO HIROSE, KAZUHIDE TSUYA, TATSUYA NISHIGAKI, EIICHI IDAKA, and SHINICHI YANO, 1989, *Liq. Crystals*, **4**, 653.
[13] VORA, R. A., and PATEL, J. P., 1985, 22nd Annual Convention of Chemists, Raipur, India.
[14] CHUDGAR, N. K., and SHAH, S. N., 1989, *Liq. Crystals*, **4**, 661.
[15] DHAR, D. N., 1981, *The Chemistry of Chalcones and Related Compounds* (Wiley).
[16] SATHE, V. R., and VENKATRAMAN, K., 1949, *Curr. Sci.*, **18**, 373.
[17] IYER, R. N., and VENKATRAMAN, K., 1951, *Proc. Ind. Acad. Sci.* A, **33**, 116.
[18] KAGAL, S. A., KARMARKAR, S. S., and VENKETRAMAN, K., 1956, *Proc. Ind. Acad. Sci.* A, **44**, 36.
[19] DAVE, J. S., and VORA, R. A., 1970, *Liquid Crystals and Ordered Fluids*, Vol. I, edited by J. F. Johnson and R. S. Porter (Plenum), p. 477.
[20] THAKKAR, D. M., 1984, Ph.D. Thesis, M.S. University of Baroda.