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New fluorescent mesogens with a chalcone central linkage

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Mesogens with a chalcone central linkage are rare. It is believed that the chalcone linkage is not conducive to mesomorphism. In the present study two homologous series were synthesized having the chalcone as a central linkage. 4-*n*-alkoxy-4′-hydroxy chalcones do not exhibit mesomorphism, however, higher members of 4-*n*-alkoxy-4′(4″-*n*-octyloxybenzoyl) chalcones, exhibit mesomorphism. The fluorescent behaviour of the chalcones is evaluated. All the compounds are characterized by standard methods.

1. Introduction

Mesogens with different central linkages are known [1]. However most of these central linkages have an even number of linking groups. The chalcone linkage has an odd number of atoms. Moreover, very few low molecular mesogens with the chalcone linkage are known, although recently, Vora *et al.* [2] have reported mesogenic polymers with a chalcone central linkage. In view of the rarity of mesogens with the chalcone linkage and their potential as fluorescent compounds, which can enhance the efficiency of solar cells, it was proposed to synthesize and study a homologous series having a chalcone central linkage.

2. Experimental

Microanalysis of compounds was performed on Coleman instrument. U.V. spectra were recorded on Shimadzu U.V. VIS 240. I.R. spectra were recorded on Shimadzu IR-408. 90 MHz N.M.R. spectra were recorded on Perkin-Elmer R-32. Mass spectra were recorded using Kratos MS 25 Spectrometer. Column Chromatography was done on Acme's Silica Gel (60–120 mesh) and spots were examined in iodine vapour. Liquid Crystalline properties were investigated on Letiz-Ortholux-II polarizing microscope provided with heating stage. Fluorescent spectra were recorded on Amino-Bowman Spectrophotometer (U.S.A.)

p-Hydroxy benzoic acid (BDH), *p*-hydroxy benzaldehyde (Fluka), *p*-hydroxy acetophenone (Bochringer) and *n*-alkyl bromide (Fluka) were used for the synthesis. The synthetic route is illustrated in figure 1.

The following steps were used for the synthesis of new compounds.

p-*n*-Alkoxy benzaldehyde [3], *p*-*n*-octyloxybenzoic acid [4] and *p*-*n*-octyloxy benzoyl chloride [4] were prepared by the reported methods.

2.1. *Procedure*

2.1.1. *Preparation of 4-n-alkoxy-4′-hydroxy chalcones*

Appropriate 4-*n*-alkoxy benzaldehydes (0·01 mole) and 4-hydroxy acetophenone (0.01 mole) were taken in a round bottom flask and were dissolved in methanol, KOH

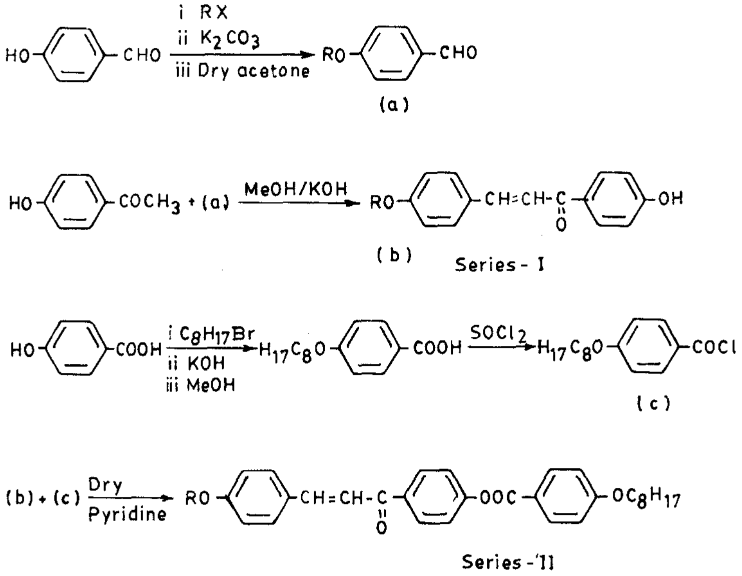


Figure 1. Synthetic route to series I and II.

solution (0·36 mole) prepared in minimum quantity of methanol, was added to above solution with stirring. The product was added to cold HCl solution with stirring. Separated product was filtered and dried. Chalcones were purified by column chromatography. The purified products were crystallized from petroleum ether–ethyl acetate mixture. The melting points of all the compounds are recorded in table 1.

Table 1. Melting points of 4-*n*-alkoxy-4′-hydroxy chalcones (Series I).

Compound No.	*n*-alkyl group	Melting points °C
1	Methyl	200·0
2	Ethyl	140·0
3	Propyl	170·0
4	Butyl	157·0
5	Pentyl	117·0
6	Hexyl	146·0
7	Heptyl	115·0
8	Octyl	144·0
9	Nonyl	110·0
10	Decyl	139·0
11	Dodecyl	110·0
12	Tetradecyl	115·0
13	Hexadecyl	105·0

2.1.2. *Preparation of 4-n-alkoxy-4′(4″-n-octyloxybenzoyl) chalcones*

4-*n*-octyloxybenzoyl chloride [4] prepared separately was added to a cold solution of appropriate 4-*n*-alkoxy-4′-hydroxy chalcone dissolved in 10 ml of pyridine with stirring. The whole mass was allowed to stand overnight at room temperature. The mixture was then poured in 1 : 1 ice cold HCl solution. The separated solid was

Table 2. Melting points and transition temperatures 4-*n*-alkoxy-4′(4″-*n*-octyloxybenzoyl) chalcones (Series-II).

Compound	*n*-alkyl group *R*	Transition temperature/°C	
		Nematic	Isotropic
1	Methyl	—	120·0
2	Ethyl	—	142·0
3	Propyl	—	128·0
			127·0†
4	Butyl	—	132·0
5	Pentyl	—	122·0
			121·5†
6	Hexyl	(101·0)	125·0
7	Heptyl	(103·0)	120·0
8	Octyl	(105·0)	119·0
9	Nonyl	(100·0)	113·5
10	Decyl	(104·0)	113·0
		100·5†	111·0†
11	Dodecyl	(102·5)	107·0
		101·0†	106·0†
12	Tetradecyl	(95·0)	101·0
13	Hexadecyl	(80·0)	87·0
		76·0†	84·5†

Values in the parenthesis indicates monotropy.
† Indicates transition temperatures obtained from D.S.C.

filtered, washed with water and dried. The esters were purified by using column chromatography and crystallized from petroleum ether. The melting points and transition temperatures are reported in table 2.

3. Results and discussion

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

Spectral analysis of the 4-*n*-alkoxy-4′-hydroxy chalcones.

U.V. ($CHCl_3$): λ_{max} 240, 320 nm.

I.R. (KBr): ν 3500–3000, 2900, 1650, 1600, 1290 cm^{-1}.

N.M.R. (90 MHz, $CDCl_3$(Compound No.:- 3 table 1: δ, 7·95 (*d*, J = 9 Hz, 2H, aromatic H), 7·6–7·45 (complex m, 5H).6·9 (*d*, superimposed with other vinyl signal, total 3H, aromatic H, vinylic H), 4·0 (*t*, J = 8 Hz, 2H, O–CH_2), 1·9 (m, 2H, CH_2), 1·5 (t, 3H, CH_3).

N.M.R. (90 MHz, $CDCl_3$) Compound No. 11 table 1: δ, 7·9 (*d*, J = 9 Hz, 2H, aromatic H), 7·6 (*d*, J = 9 Hz, 2H, aromatic H), 7·4 (*d*, J = 4·5 Hz, 1H, olefin H), 7·2 (*d*, J = 4·5 Hz, 1H, olefin H), 6·9–6·8 (m, 4H, aromatic H), 6·6 (en, 1H, OH), 3·9 (*t*, 2H, O–CH_2), 1·7–1·2 (br, 2OH, methylenes), 0·9 (*t*, 3H, CH_3).

Mass spectrum was recorded for compound No. 1 table 1: m/e 254 (M^+, base peak), 239, 223, 221, 161, 121, 108, 93, 77, 65, 28.

The fluorescence pattern was studied for compound No. 8, table 1.

It has been observed that there are three excitation peaks at 232, 260 and 288 nm. For the above excitation wave lengths when the emission spectra has been studied, the emission takes place at 344 and 484 nm. Moreover, the intensity of peak at 484 nm emission is nearly equal at 232 and 288 nm excitation, while that at 260 nm was lower. The emission observed at 344 nm is comparatively much smaller than that of 484 nm emission peak.

Spectral analysis of the 4-*n*-alkoxy-4′-(4″-*n*-octyloxy benzoyl) chalcones.

U.V. ($CHCl_3$): λ_{max} 274, 320 nm.

I.R. (KBr): ν 2900, 1730, 1660, 1600, 1295 cm^{-1}.

N.M.R. (90 MHz, $CDCl_3$), Compound No. 3, table 2: δ, 8·0 (m, 4H, aromatic H), 7·6–7·2 (m, 6H, vinylic and aromatic H), 6·9 (m, 5H, aromatic H), 4·0 (two triplets, superimposed, 4H, O–CH_2s), 1·9 (br, 4H, CH_2s), 1·5–1·0 (m, 16H, CH_2s and CH_3s).

N.M.R. (90 MHz, $CDCl_3$), Compound No. 11, table 2: δ, 8·0 (two *d*, $J = 7$ Hz, 4H, aromatic H), 7·7–7·25 (series of *d*, 6H, aromatic H and vinylic H), 7·0–6·9 (two *d*, $J = 7$ Hz, 4H, aromatic H), 4·00 (two superimposed *t*, 4H, O–CH_2s), 1·8–1·2 (br, 33H, CH_2s), 1·0 (brt, 6H, methyl H).

Mass spectrum was recorded for compound No. 1, table 2: m/e 486 (M^+, base peak), 388, 375, 254, 233, 221, 165, 121, 93, 65, 43, 20.

The fluorescence pattern was studied for compound No. 8, table 2.

Three excitation peaks were observed at 232, 248 and 280 nm. For the above excitation wave lengths when the emission spectra has been studied, the emission peak at 480 nm have been marked. Moreover, the intensity of peak at 480 nm emission is comparatively high at 280 nm excitation than that of the 232 and 248 nm.

The detailed study of the fluorescence, of all compounds of tables 1 and 2 is under current investigation and will be published later.

4. 4-n-alkoxy-4′-hydroxy chalcones

The melting points of the compounds of Series-I are recorded in table 1. It shows that Series-I is non-mesogenic. The liquid crystalline property was checked with special care so that no phase was missed. Non-mesomorphism was also confirmed by taking DTA for few samples.

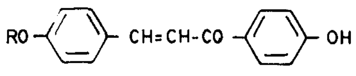
Gray [1] had explained the non-mesomorphism of phenolic compounds on the basis of strong intermolecular hydrogen bonding in such molecules which raises melting points above the mesomorphic–isotropic liquid transition temperature. It may also encourage a non-linear structural arrangement which is a deterrent to mesomorphism.

Nguyen *et al.* [5] have reported that a ketonic group linking two phenyl rings (benzophonene derivatives) is non-conducive to mesomorphism due to the angular shape of such molecules resulting from the angle of keto group.

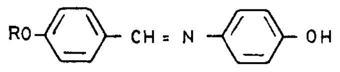
It would be quite interesting to correlate the mesogenic properties of Series-I with other related homologous series. The geometry and mesogenic behaviour of Series-I is compared with those of Series-*A* [6], *B* [7], *C* [6] and *D* [8].

Reference to the geometry indicates that Series-*A*, *B* and *C* differ only in the central linkages, Series-*A* and *B* have azomethine and ester central linkages respectively.

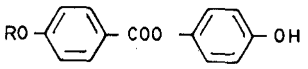
As mentioned above, non-mesomorphism of Series-*A* and *B* is attributed to the presence of phenolic terminal group which leads to intermolecular hydrogen bonding.



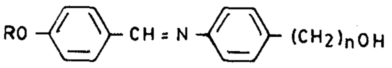
Series-1 (Non-Mesogenic)



Series-A (Non-Mesogenic)

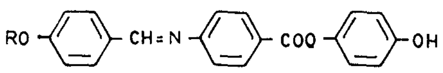


Series-B (Non-Mesogenic)



Series-C (Mesogenic)

Where n=1 and 2



Series-D (Mesogenic)

This comparison does not give proper perspective as Series-I has –CH=CH–CO– as a central linkage, which is also non-conducive to mesomorphism. It may be the combined effect of both forces which affected mesomorphism.

However, reference to Series-*C* indicates that if –OH is shifted from the aromatic nucleus, the system exhibits mesomorphism. This supports the above view that strong intermolecular hydrogen bonding destroys the mesomorphism: By shifting the –OH group away from phenolic terminal group the molecules of Series-*C* will have very weak hydrogen bonding due to the aliphatic hydroxy group.

Reference to the geometry of Series-*D* indicates that, although a terminal phenolic group is present, the system exhibits mesomorphism. This shows that mesomorphism is not only dependent on the terminal phenolic group. Incorporation of one phenyl ring and azomethine linkage resulted in a mesogenic system.

5. 4-n-alkoxy-4′(4″-n-octyloxybenzoyl) chalcones

The transition temperature of the Series-II are recorded in table 2.

From hexyloxy onwards, all the derivatives exhibit a monotropic nematic phase. The transition temperatures exhibit an odd–even effect for the nematic–isotropic transition temperature as shown in figure 2.

The nematic–isotropic transition temperature falls as the series is ascended. The solid–isotropic transition temperatures also exhibit an odd–even effect.

The average thermal stabilities of Series-II are compared with related homologous series as shown in figure 3.

The reference to average thermal stabilities (table 3) shows that Series-II is less stable compared to homologous Series-*C* and *D*. Only few members of homologous Series-*A* and *B* are reported.

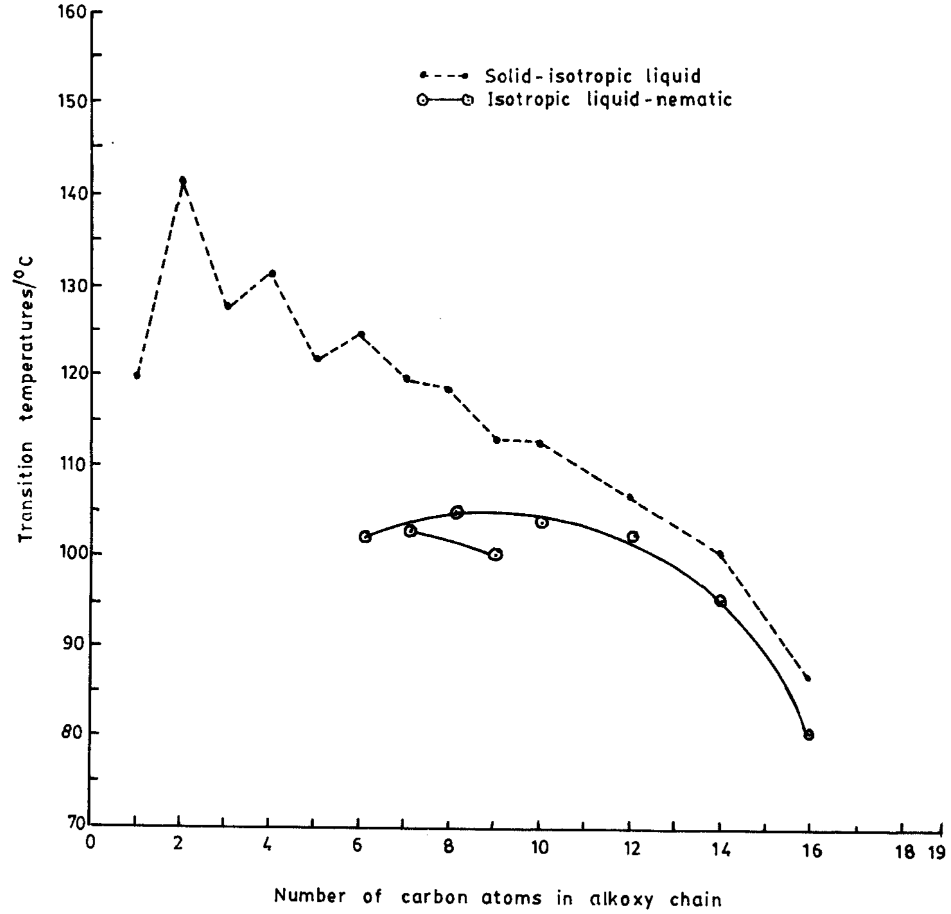


Figure 2. Graph of transition temperature versus number of carbon atoms in alkoxy chain.

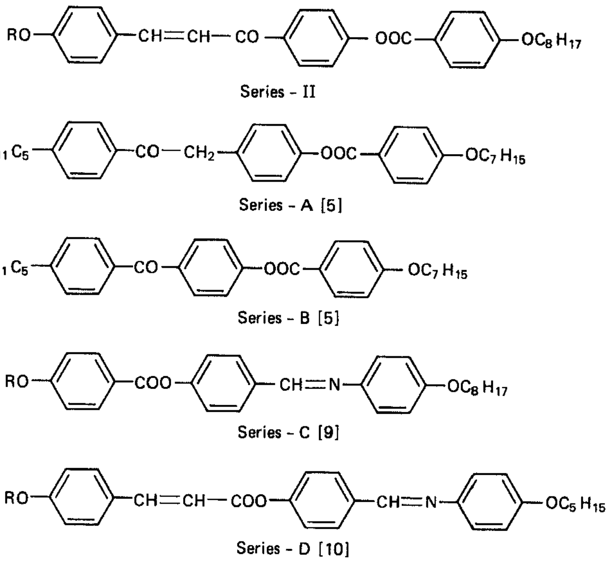


Figure 3.

Table 3. Average thermal stabilities.

	Series				
	II	*A*	*B*	*C*	*D*
Nematic–isotropic or isotropic–nematic C_6, C_7, C_8, C_{10}, C_{12}	103·1	113·5	Non-mesogenic	169·2	168·8
Commencement of smectic-phase	—	C_7	—	C_5	C_5

The mesomorphism begins from hexyloxy derivative onwards in Series-II. It is monotropic nematic in nature. The reference to geometry of molecules of Series-II and *A* indicates that the molecules of both the series have many common features. Both the series have terminal alkoxy group, one central ester linkage and the keto group in the second central linkage. However they differ in the terminal group and the central linkage. Both of the series exhibit monotropic nematic phases from the middle members onward. This shows that the minor changes in the terminal group and the difference of number of atoms in one of the central linkage does not affect the mesogenic properties markedly.

The molecules of Series-*B* have a keto central linkage, whereas the other factors are similar to Series-II. The aryl rings in Series-*B* (having keto group) cannot be colinear because of the geometry of linking groups. In such systems a colinear arrangement would introduce unacceptable angle strain. Naturally the structure will be non-conducive to mesomorphism, hence Series-*B* is non-mesogenic.

Reference to the geometry indicates that the difference in Series-II and *C* is only in one central linkage. Series-II has –CH=CH–CO– central linkage whereas Series-*C* has –CH=N– central linkage. The nematic thermal stability of Series-*C* is higher than that of Series-II; The –CH=N– group is known to be more conducive to mesomorphism compared to –CH=CH–CO group [11]. Naturally it will have higher thermal stability. Series-*C* exhibits smectic phases whereas Series-II is nematogenic.

Series-*D* also has higher thermal stability compared to Series-II. Both of the central linkages of Series-*D* are more conducive to mesomorphism compared to Series-II.

These comparisons have brought out the fact that –CH=CH–CO– linkage is less conducive to mesomorphism compared to –CH=N–, –COO– linkages due to the non-linearity and angle strain arising from the keto group. The study has provided, for the first time, mesogenic compounds with chalcone linkage. They exhibit fluorescent properties.

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