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N. K. Chudgar^a; Alpana Shah^a

^a Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda, India

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Synthesis and study of mesogenic compounds having a methylene ketone ($-\text{CH}_2-\text{CO}-$) linking group

by N. K. CHUDGAR* and ALPANA SHAH

Department of Chemistry, Faculty of Science,
M.S. University of Baroda, Baroda-390 002, India

Recently we have reported isoflavone derivatives as potential mesogens [1]. During the synthesis of isoflavone derivatives, 2,4-dihydroxyphenyl benzyl ketone was synthesized as an intermediate. Nguyen Huu Tinh *et al.* [2] have reported the effect of the influence of the central linkage, such as ethylene, methylene ketone and ketone on the mesogenic compounds. Vora *et al.* [3] have also reported a mesogenic homologous series with terminal and lateral phenolic groups. To understand the effect of hydrogen bonding originating between methylene ketone and free lateral hydroxy groups, *ortho* to the methylene ketone group, on mesogenicity, the present homologous series of 2-hydroxy, 4(4'-*n*-alkoxybenzoyloxy)phenyl benzyl ketone was synthesized. The synthesized compounds were characterized by elemental analysis and spectroscopic techniques. The first six homologues of the present series are non-mesogenic and mesomorphism appears from the heptyl derivative onwards. The present series shows a monotropic smectic A phase except for the last member (octadecyloxy) which exhibits an enantiotropic smectic A mesophase. The transition temperatures are also identified using DSC. The fluorescent studies of some of the compounds of the present series are under investigation.

1. Introduction

Mesogenic systems with a carbonyl as part of a linkage group are rare. The carbonyl group normally imparts non-linearity to the molecules which is not conducive to mesomorphism. However it has been pointed out that if a carbonyl group is 'locked' by a phenolic group through hydrogen bonding then there is a possibility of mesomorphism [4]. Nguyen *et al.* [2] have reported that a carbonyl group linking two phenyl rings (benzophenone derivatives) is non-conducive to mesomorphism due to the angular shape of such molecules resulting from the geometry of the carbonyl group.

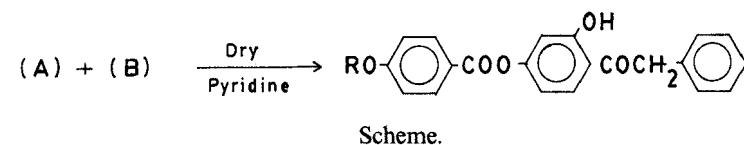
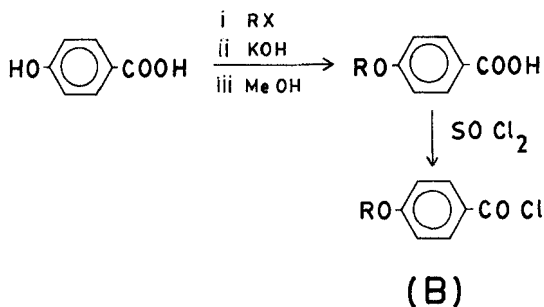
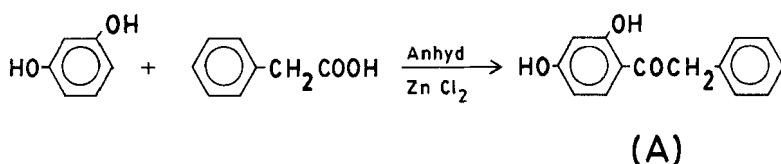
In the present study it was proposed to synthesize a homologous series having a hydroxy group *ortho* to the carbonyl group in the central linkage.

2. Experimental

Microanalyses of compounds were performed on a Coleman instrument. IR spectra were recorded on a Shimadzu IR-408 and 90 MHz NMR spectra on a Perkin-Elmer R-32. Liquid crystalline properties were investigated with a Leitz-Laborlux polarizing microscope provided with a heating stage. DSC analyses were investigated on a Mettler TA 4000 system.

4-Hydroxybenzoic acid (BDH), the appropriate alkyl halides (B.D.H.), resorcinol (Sisco-chem), and phenylacetic acid (Sisco-chem) were used for the synthesis. The synthetic route is illustrated in the scheme. The 4-*n*-alkoxybenzoic acids, 4-*n*-alkoxybenzoyl chloride and benzyl 2,4-dihydroxyphenyl ketone were prepared according to reported methods [5, 6].

* Author for correspondence.



2.1. Procedure

The general preparation of the benzyl 2-hydroxy-4-(4'-*n*-alkoxybenzoyloxy)phenyl ketones is as follows. Benzyl 2,4-dihydroxyphenyl ketone (0.02 mol) was dissolved in dry pyridine (5 ml) and a cold solution of a 4-*n*-alkoxybenzoyl 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. The solid which separated was filtered off and recrystallized from ethanol.

The elemental analyses of all the compounds were found to be satisfactory.

Spectral analysis of benzyl 2-hydroxy-4-(4'-*n*-alkoxybenzoyloxy) phenyl ketones.

- (i) The IR (KBr) spectra of the compounds showed the characteristic -OH stretching frequency at 2850 cm^{-1} due to the formation of the chelated structure. The carbonyl band was seen at 1740 cm^{-1} . Other signals observed were at 2950 , 1610 , 1260 cm^{-1} .
- (ii) NMR spectrum (90 MHz, CDCl_3) of compound **10** (see table 1). A singlet far downfield at 12.55 p.p.m. for the chelated hydroxy proton was exhibited. The aromatic protons were seen as a multiplet, 6.9–8.1 p.p.m. for twelve protons, and a singlet at 4.2 p.p.m. (2 H) for the benzylic protons. The signal at 4.0 p.p.m. was diagnostic of the $-\text{OCH}_2$ of the alkoxy group. The remaining alkyl protons (16 H) were observed in the region 1.6–1.05 p.p.m.
- (iii) NMR spectrum (90 MHz, CDCl_3) of compound **9** (see table 1). The corresponding values for this compound are: 13.0 (s, 1 H, chelated hydroxy proton), 15–6.8 (m, 12 H, aromatic protons), 4.25 (s, 2 H), COCH_2Ph , 4.0 (t, 2 H, $-\text{OCH}_2$), 1.35 (14 H, methylene), 0.95 p.p.m. (m, 3 H, CH_3).

Table 1. The benzyl 2-hydroxy-4-(4'-*n*-alkoxybenzoyloxy)phenyl ketones.

Compound no.	<i>R</i>	Transition temperatures (°C)	
		Smectic	Isotropic
1	Methyl	—	108
2	Ethyl	—	136
3	Propyl	—	136
4	Butyl	—	140
5	Pentyl	—	113
6	Hexyl	—	118
7	Heptyl	(63)	70
8	Octyl	(61)	94
9	Nonyl	(69)	82
10	Decyl	(71)	79
11	Dodecyl	(74)	80
12	Tetradecyl	(76)	82
13	Hexadecyl	(79)	87
14	Octadecyl	74	86

Values in parentheses indicate monotropic transition.

Table 2.

Compound no.	Heating rate/K min ⁻¹	Peak temperature	$\Delta H/\text{J g}^{-1}$	$\Delta S/\text{J g}^{-1} \text{K}^{-1}$	Total $\Delta S/\text{J g}^{-1} \text{K}^{-1}$
8	10	C 93.3(94)† I	136.36	0.3722	0.4128
		I 50.8(61)† S	13.799	0.0426	
12	10	C 85.1(82)† I	110.06	0.3072	0.3457
		I 72.5(76)† S	11.940	0.0345	
14	10	K 68.3(74)† S	5.9695	0.0173	0.3272
		S 85.2(86)† I	111.02	0.3099	

† Indicates transition temperatures observed under the microscope.

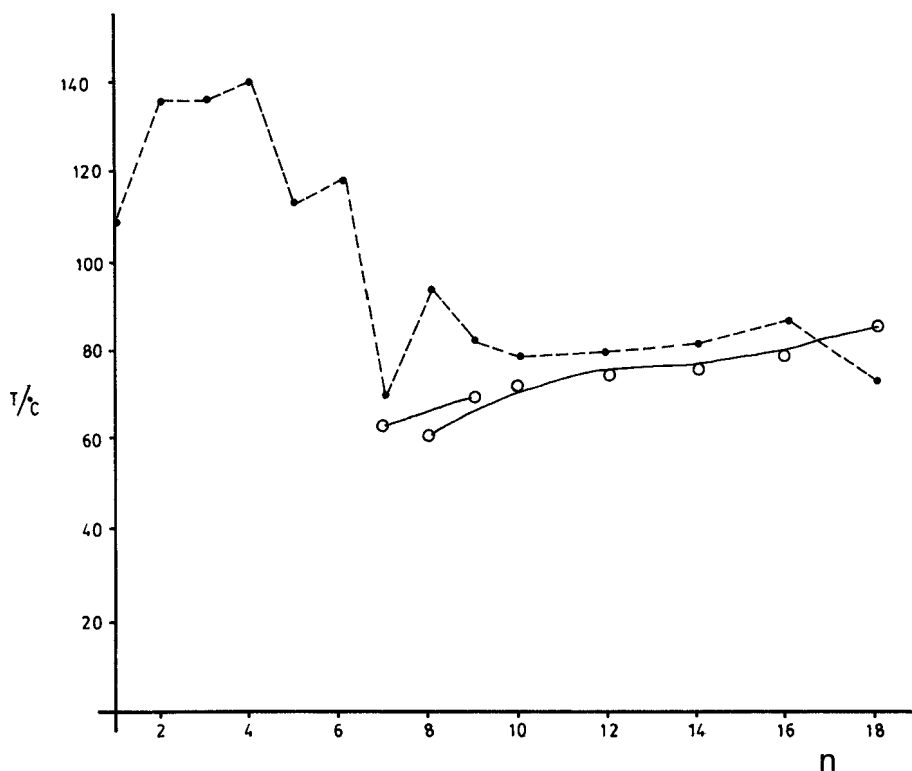
3. Results and discussion

The transition temperatures for the compounds studied are compiled in table 1 and DSC data of some of the compounds listed are given in table 2.

The first six homologues are non-mesogenic. Mesomorphism appears from the heptyl derivative onwards. The present series shows monotropic smectic A phases except for the last member which has an enantiotropic smectic A phase.

The plot of the number of carbon atoms in the alkoxy chain versus the transition temperatures exhibits an odd-even effect for the smectic-isotropic transition temperatures (see the figure). The gradient of the rising smectic-isotropic transition temperature curve becomes less steep as the number of carbon atoms in the alkoxy chain increases. The odd-even effect in the smectic-isotropic transition temperatures has also been observed by other workers [7-10].

The mesomorphism exhibited by the present system is of some interest to understand the effect of different structural aspects on mesomorphism in particular the molecular geometry.



The transition temperatures versus the number of carbons in the alkoxy chain, n . ● Crystal to mesophase or isotropic and ○ smectic to isotropic transitions.

Table 3.

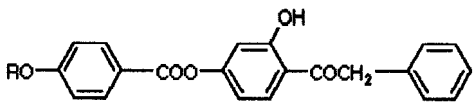
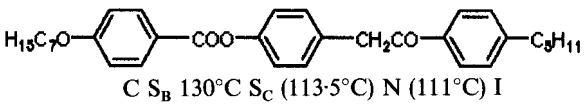
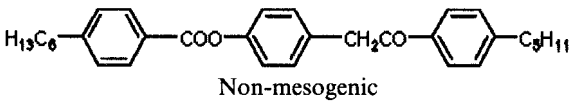
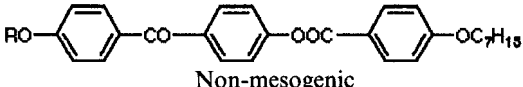
 <p>Mesogenic for $R > C_6H_{13}$</p>	Present series 1
 <p>C S_B 130°C S_C (113.5°C) N (111°C) I</p>	Compound A [2]
 <p>Non-mesogenic</p>	Compound B
 <p>Non-mesogenic</p>	Series C

Table 3 compares the present series 1 with compound A. Series 1 is devoid of a terminal alkyl group whereas compound A does not possess a lateral hydroxy group *ortho* to the carbonyl group. Not only this, but the carbonyl group is attached to the central phenyl ring in series 1 whereas it is attached to the terminal phenyl ring in the case of compound A. Both systems have monotropic mesophases.

The heptyloxy homologue of series 1 has a monotropic smectic–isotropic transition (57°C) which is very low compared to the transitions reported for compound A. This may be attributed to the presence of the lateral hydroxy group and to the absence of the terminal phenyl group in series 1. The lateral hydroxy group increases the breadth of the molecules of series 1. It is known that an increase in molecular breadth adversely affects phase thermal stability. The absence of a terminal group also reduces the mesogenic properties of the system. Due to these two factors the average mesomorphic thermal stability of series 1 is much lower compared to that of compound A. The absence of mesomorphism in compound B and C series indicates that the presence of carbonyl group in the linkage is not conducive to mesomorphism; either it requires a long alkoxy terminal group as is present in series A or a lateral hydroxy group *ortho* to the carbonyl group thereby giving rise to hydrogen bonding and decreasing the adverse effect of the carbonyl group. This indicates that appropriately designed molecules can exhibit mesomorphism.

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