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Mesomorphic Heterocyclic Homologous Series: 1.7-(4'-n-Alkoxybenzoyloxy)-3-acetylcoumarins 11. 4'-Formylphenyl 7-n- alkoxycoumarin-3-carboxylates

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Mesomorphic Heterocyclic Homologous Series: I. 7-(4′-*n*-Alkoxybenzoyloxy)-3-acetylcoumarins II. 4′-Formylphenyl 7-*n*-alkoxycoumarin-3-carboxylates

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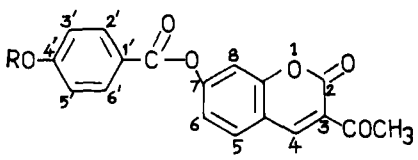
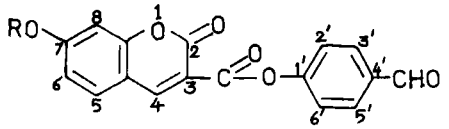
Two homologous series of coumarin derivatives have been synthesized and mesomorphic behavior of their members has been studied. In case of Series I, mesomorphism does not begin to appear until the butyl homolog, which is monotropic nematic. The remaining members of the series exhibit both nematic and smectic or only smectic properties. In case of Series II, all the homologs, except the first seven, exhibit only a smectic phase. In both the series, plots of S–N or I transition temperatures versus the number of carbon atoms in the alkoxy chain show an ascending tendency.

1. INTRODUCTION

A few workers have reported mesomorphic nitrogen heterocycles in the recent past.[1-3] Young *et al.*[4] and Dewar *et al.*[5] have prepared several compounds containing five membered as well as six membered heterocyclic rings and have discussed the effect of heterocyclic ring on mesomorphic behavior. Literature survey also reveals that two series containing oxygen as hetero atom are reported.[6,7] In order to study the effect of coumarin moiety on liquid crystal behavior, two series of compounds having the following general structure are synthesized.



SERIES I



SERIES II

2. RESULTS

Series I. 7-(4'-*n*-Alkoxybenzoyloxy)-3-acetylcoumarins

Melting points and transition temperatures of the compounds synthesized are compiled in Table I. The first three homologs of the series are non-mesomorphic; mesomorphism appear at the butyl derivative which is monotropic nematic. The smectic phase commences from the pentyl derivative which exhibits both smectic and nematic as monotropic phases. The hexyl derivative shows monotropic smectic and enantiotropic nematic properties. Only enantiotropic smectic phase is observed beyond hexyl homolog. Figure 1 shows the relationship of transition temperatures to carbon numbers in the alkoxy chain. Smectic-Nematic or Isotropic transition points show ascending tendency without odd-even alternation.

Series II. 4'-Formylphenyl 7-*n*-alkoxycoumarin-3-carboxylates

Melting points and transition temperatures of the compounds of this series are reported in Table II. Mesomorphism does not begin to appear until the octyl

TABLE I

7-(4'-*n*-Alkoxybenzoyloxy)-3-acetylcoumarins.

Compound	*n*-Alkyl group	Transition Temperature (°C) Smectic	Nematic	Isotropic
1	Methyl	—	—	198.0
2	Ethyl	—	—	196.0
3	Propyl	—	—	175.5
4	Butyl	—	(143.5)	145.5
5	Pentyl	(129.0)	(141.0)	142.0
6	Hexyl	(138.5)	143.0	145.5
7	Heptyl	129.5	—	146.5
8	Octyl	129.0	—	151.0
9	Nonyl	123.0	—	154.5
10	Decyl	120.0	—	157.5
11	Dodecyl	117.0	—	159.5
12	Tetradecyl	116.5	—	160.0
13	Hexadecyl	115.5	—	158.5
14	Octadecyl	112.5	—	157.0

Values in the parentheses indicate monotropy.

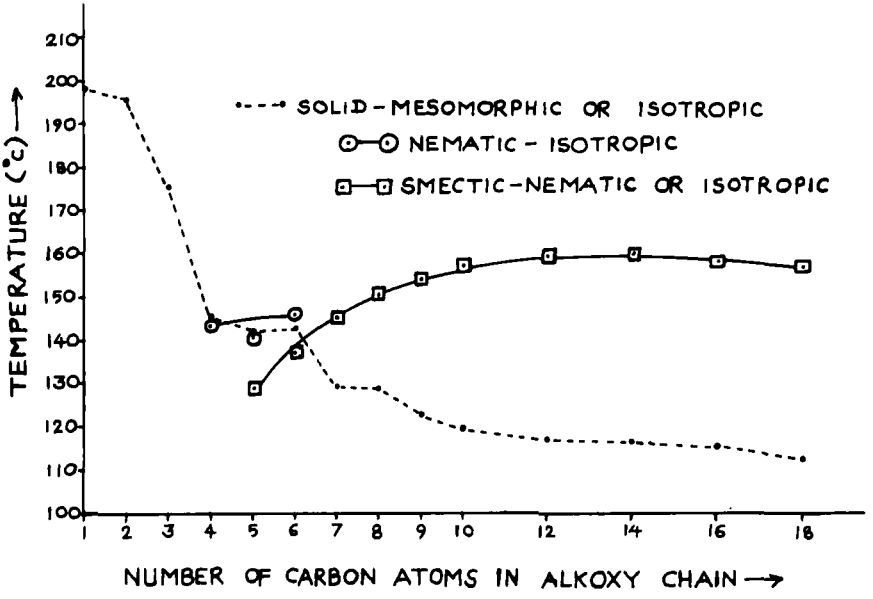


FIGURE 1 7-(4'-*n*-Alkoxybenzoyloxy)-3-acetylcoumarins.

TABLE II

4'-Formylphenyl 7-*n*-alkoxycoumarin-3-carboxylates.

Compound	*n*-Alkyl group	Transition Temperature (°C) Smectic	Isotropic
15	Methyl	—	194.5
16	Ethyl	—	201.0
17	Propyl	—	179.5
18	Butyl	—	162.5
19	Pentyl	—	162.0
20	Hexyl	—	170.0
21	Heptyl	—	157.5
22	Octyl	(135.5)	153.5
23	Nonyl	(143.0)	147.0
24	Decyl	143.0	148.5
25	Dodecyl	134.5	157.5
26	Tetradecyl	137.0	164.0
27	Hexadecyl	136.0	166.0

Values in the parentheses indicate monotropy.

homolog. The octyl and the nonyl derivatives are monotropic smectic; whereas the remainder exhibit only an enantiotropic smectic phase. Figure 2 shows the plot of transition temperatures versus the number of carbon atoms in the alkoxy chain. Smectic–Isotropic transition points lie on a rising curve.

In Series I, only the nematic phase of pentyl and hexyl homologs adopt a homeotropic texture on cooling the isotropic liquid. On cooling the nematic melt, in both the cases, focal conic smectic phase is obtained. On heating the smectic melt, nematic phase is obtained which immediately adopts a homeotropic texture. The reversals of these transitions are sharply detectable because near the transitions (Smectic–Nematic or Nematic–Isotropic) the field becomes birefringent. In both the series, the smectrogenic compounds behave in a similar manner—on cooling the isotropic liquid, batonnets separate from it and coalesce together to form quite clear fan shaped focal conic texture in each case. In no case, a smectic phase adopting a schlieren texture has been observed. For both the series, in case of compounds exhibiting only smectic phase, homeotropy is not observed.

During the synthesis of the present Series II, two precursor series, viz. (i) Ethyl 7-*n*-alkoxycoumarin-3-carboxylates and (ii) 7-*n*-alkoxycoumarin-3-carboxylic acids have been synthesized. Both the series, even the latter, did not show mesomorphic property. It may be noted that the members of the series 6-*n*-alkoxy-2-naphthoic acids,[8] geometrically related to the latter, show mesomorphic properties. Gray[8] has proposed that the dimerisation of the acid molecules is responsible for the mesomorphic properties exhibited by them. In

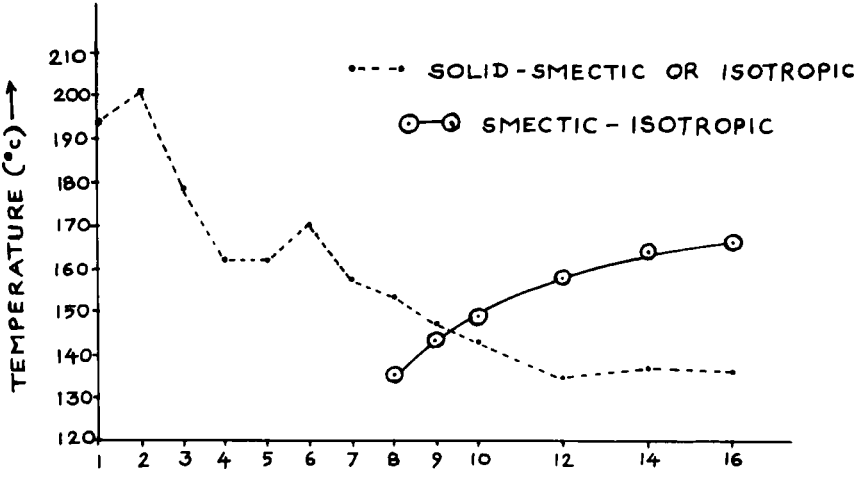


FIGURE 2 4′-Formylphenyl 7-*n*-alkoxycoumarin-3-carboxylates.

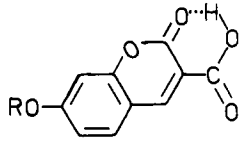


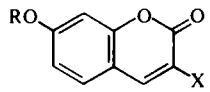
FIG.3

case of 7-*n*-alkoxycoumarin-3-carboxylic acids, we suggest that the intramolecular hydrogen bonding (Figure 3) between the hydrogen atom of the carboxyl group and the oxygen atom of the ketonic group of lactone moiety prevents the dimer formation of the acid molecules. Therefore the members of this series are non-mesomorphic. A. I. Pavluchenko *et al.*[9] have given similar reason for the absence of mesomorphic property in their 5-alkoxynicotinic acids. The melting points of the two non-mesomorphic series are compiled in Table III.

3. EXPERIMENTAL

Melting points and transition temperatures were determined using a Leitz Ortholux Polarishing Microscope equipped with a heating stage. In the neighborhood of each phase transition, the temperature was raised at the rate of 0.5°C per minute.

TABLE III



R	m.ps. in (°C) X = —$COOC_2H_5$	X = —COOH
CH_3	134.0*[14]	195.0*[14]
C_2H_5	118.0	215.5
C_3H_7	89.0	199.5
C_4H_9	119.0	163.0
C_5H_{11}	92.0	150.0
C_6H_{13}	145.0	146.5
C_7H_{15}	144.0	145.0
C_8H_{17}	138.5	139.0
C_9H_{19}	136.5	138.0
$C_{10}H_{21}$	134.0	135.0
$C_{12}H_{25}$	132.5	133.5
$C_{14}H_{29}$	129.0	132.0
$C_{16}H_{33}$	128.5	130.0

* Known melting points.

Preparation of compounds:

Series I.

1. *p-n*-Alkoxybenzoic acids and *p-n*-Alkoxybenzoyl chlorides were prepared as described by Dave and Vora.[10]

2. *2,4-Dihydroxybenzaldehyde*: This compound was prepared according to the method of Bisagni, Buu-Hoi and Royer.[11]

3. *7-Hydroxy-3-acetylcoumarin*: It was prepared as described by Balaiah, Seshadri and Venkatswarlu.[12]

4. *7-(4'-n-Alkoxybenzoyloxy)-3-acetylcoumarins*: *p-n*-Alkoxybenzoylchloride (0.005 mol) and 7-hydroxy-3-acetylcoumarin were dissolved in pyridine and heated on a water bath for an hour. The reaction mixture was poured in dil. hydrochloric acid. The solid product was washed with dil.NaOH, water and crystallized from a mixture of ethanol and few drops of benzene. The analytical data for the compounds are given in Table IV.

Series II.

1. *Ethyl 7-hydroxycoumarin-3-carboxylate*: 2,4-Dihydroxybenzaldehyde (0.1 mol), diethyl malonate (0.1 mol), 15 ml of dry pyridine and a few drops of piperidine were mixed and left overnight. The reaction mixture was decomposed by dil. hydrochloric acid. The product was washed with water and crystallized from ethanol (m.p. found: 170°C., reported[13]: 171°C).

2. *Ethyl 7-n-Alkoxycoumarin-3-carboxylates*: Ethyl 7-hydroxycoumarin-3-carboxylate (0.01 mol), *n*-alkyl bromide or iodide (0.012 mol), potassium carbonate (0.07 mol) and 15 ml. of dimethyl formamide were mixed and heated on steam bath for 20 hrs. The reaction mixture was decomposed on crushed ice. The product was washed with water and crystallized from ethanol or acetic acid. All the compounds show satisfactory elemental analyses.

3. *7-n-Alkoxycoumarin-3-carboxylic acids*: Ethyl 7-*n*-alkoxycoumarin-3-carboxylate (0.01 mol) was dissolved in 40 ml. 10% alcoholic potassium hydroxide and left overnight. The reaction mixture was decomposed by ice cold dil. hydrochloric acid. The product was washed with water and crystallized from ethanol or acetic acid. All the compounds show satisfactory elemental analyses.

4. *4'-Formylphenyl 7-n-alkoxycoumarin-3-carboxylates*: The corresponding 7-*n*-alkoxycoumarin-3-carboxylic acids were treated with excess of thionyl chloride and 7-*n*-alkoxycoumarin-3-carboxylic acid chlorides thus prepared were treated with equimolar quantities of *p*-hydroxybenzaldehyde (0.005 mol) in 5-7 ml of dry pyridine and heated on water bath for an hour and left overnight. The reaction mixture was then added to ice cold dil. hydrochloric acid. The product was washed with dil. NaOH, water and crystallized from a mix-

TABLE IV

Compound	Molecular formula	% required C	% required H	% found C	% found H
1	$C_{19}H_{14}O_6$	67.45	4.14	67.28	4.38
2	$C_{20}H_{16}O_6$	68.19	4.55	68.08	4.37
3	$C_{21}H_{18}O_6$	68.85	4.92	69.23	5.15
4	$C_{22}H_{20}O_6$	69.47	5.26	69.31	5.18
5	$C_{23}H_{22}O_6$	70.04	5.58	69.60	5.55
6	$C_{24}H_{24}O_6$	70.58	5.88	70.50	6.09
7	$C_{25}H_{26}O_6$	71.09	6.16	70.60	6.02
8	$C_{26}H_{28}O_6$	71.57	6.42	71.74	6.05
9	$C_{27}H_{30}O_6$	71.99	6.67	71.91	6.22
10	$C_{28}H_{32}O_6$	72.41	6.90	72.39	6.73
11	$C_{30}H_{36}O_6$	73.16	7.32	73.14	6.92
12	$C_{32}H_{40}O_6$	73.84	7.69	73.52	7.44
13	$C_{34}H_{44}O_6$	74.46	8.03	74.25	7.65
14	$C_{36}H_{48}O_6$	75.01	8.33	74.62	8.24
15	$C_{18}H_{12}O_6$	66.67	3.70	66.42	3.77
16	$C_{19}H_{14}O_6$	67.46	4.14	67.00	4.16
17	$C_{20}H_{16}O_6$	68.18	4.55	67.70	4.48
18	$C_{21}H_{18}O_6$	68.85	4.92	68.89	4.92
19	$C_{22}H_{20}O_6$	69.47	5.26	69.00	5.15
20	$C_{23}H_{22}O_6$	70.05	5.58	69.92	5.40
21	$C_{24}H_{24}O_6$	70.59	5.88	70.28	5.75
22	$C_{25}H_{26}O_6$	71.09	6.16	70.84	5.92
23	$C_{26}H_{28}O_6$	71.56	6.42	72.04	6.29
24	$C_{27}H_{30}O_6$	72.00	6.67	71.88	6.28
25	$C_{29}H_{34}O_6$	72.80	7.11	72.90	7.37
26	$C_{31}H_{38}O_6$	73.52	7.51	73.13	7.26
27	$C_{33}H_{42}O_6$	74.16	7.87	73.87	7.81

ture of ethanol containing few drops of benzene. The analytical data of the compounds are given in Table IV.

References

1. H. Zaschke, K. Nitsche and H. Schubert., *J. Prakt. Chem.*, **319(3),** 475 (1977).
2. H. Zaschke, S. Arndt, V. Wagner and H. Schubert., *Z. Chem.*, **17(8),** 293 (1977).
3. A. Boller, M. Cereghetti, M. Schadt and H. Scherrer, *Mol. Cryst. Liq. Cryst.*, **42(1-3),** 1225 (1977).
4. W. R. Young, I. Haller and L. Williams in Liquid Crystals and Ordered Fluids (Plenum Press, New York) 1970, p. 383.
5. M. J. S. Dewar, A. Griffin and R. M. Riddle in Liquid Crystals and Ordered Fluids Vol. 2 (Plenum Press, New York) 1974, p. 733.
6. H. Kelker and B. Scheurle, *J. Phys.* (Paris), Colloq., **4,** 104 (1969).
7. T. I. Zaverkova, N. F. Lyukmanov and E. I. Kovshev, *Zh. Org. Khim.*, **16,** 645 (1980).
8. G. W. Gray and B. Jones., *J. Chem. Soc.*, 683 (1954).
9. A. I. Pavluchenko, N. I. Smirnova, V. V. Titov, E. I. Kovshev and K. M. Djumaev, *Mol. Cryst. Liq. Cryst.*, **37,** 35 (1976).

10. J. S. Dave and R. A. Vora in Liquid Crystals and Ordered Fluids (Plenum Press, New York) 1970, p. 477.
11. M. Bisagni, Ng. Ph. Buu-Hoi and R. Royer., *J. Chem. Soc., 3693 (1955).*
12. V. Balaiah, T. R. Seshadri and V. Venkatswarlu., *Proc. Indian Acad. Sci.,* **16A,** 68 (1942).
13. S. Rangaswami, T. R. Seshadri and V. Venkatswarlu., *Proc. Indian Acad. Sci.,* **13A,** 316 (1941).
14. B. Wilson and (the Late) C. B. Collis., *J. Chem. Soc.,* **Suppl. issue No. 1 S12** (1949).