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p-Acylphenyl Esters of p-n-Alkoxybenzoic Acids: I. Mesomorphic Behaviour

I. I. Konstantinov [a] , Y. B. Amerik [a] , B. A. Krentsel [a] & E. V. Polunin [b]
[a] Topechiev Institute of Petrochemical Synthesis Academy of Sciences, Moscow, USSR
[b] Research Institute "SUPFIR", Moscow, USSR

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p-Acylphenyl Esters of *p*-*n*-Alkoxybenzoic Acids

I. Mesomorphic Behaviour

I. I. KONSTANTINOV, Y. B. AMERIK and B. A. KRENTSEL

Topchiev Institute of Petrochemical Synthesis
Academy of Sciences, USSR, Moscow

and

E. V. POLUNIN

Research Institute "SUPFIR", USSR, Moscow

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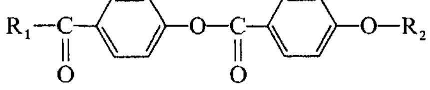
Twenty compounds belonging to the class of acylphenyl esters of *p*-*n*-alkoxybenzoic acids were synthesized. Their mesomorphic properties were studied using a polarizing microscope. These compounds form a smectic modification starting with the lower homologues. An explanation for this phenomenon is suggested.

1 INTRODUCTION

The synthesis and investigation of the physical properties of a new homologous series of liquid crystalline compounds are important in studying the relationship between the structure of molecules, their "architecture" and the characteristics of the mesomorphic state.

p-Acylphenyl esters of *p*-*n*-alkoxybenzoic acids with the general formula



where R_1 and R_2 = *n*-alkyl were prepared and their mesomorphic properties were studied. Twenty compounds were obtained which could be divided into three groups which differs with the length of the alkyl chain R_1.

p-Acylphenyl esters form in the main a smectic mesophase (see Table). The first group—*p*-acetylphenyl esters—consists of five compounds, of which two form a monotropic smectic modification (16 and 17)† and one a nematic, the other two exhibit enantiotropic smectic properties. In the second group (propionyl esters) all seven compounds form an enantiotropic mesophase; in addition three members (24, 25, 26) have a nematic and two (27 and 29) smectic modification II. In the third group (*p*-butyryl esters) the lower homologue (33) does not exhibit mesomorphism, 34 forms monotropic nematic and smectic modifications and the remaining compounds have an enantiotropic smectic modification.

As is shown in Figure 1, for all three groups of compounds there is a tendency for the clearing points to increase as the alkoxy chain becomes longer, which is generally characteristic of some nonsymmetrically *p,p*′-substituted compounds.[1]

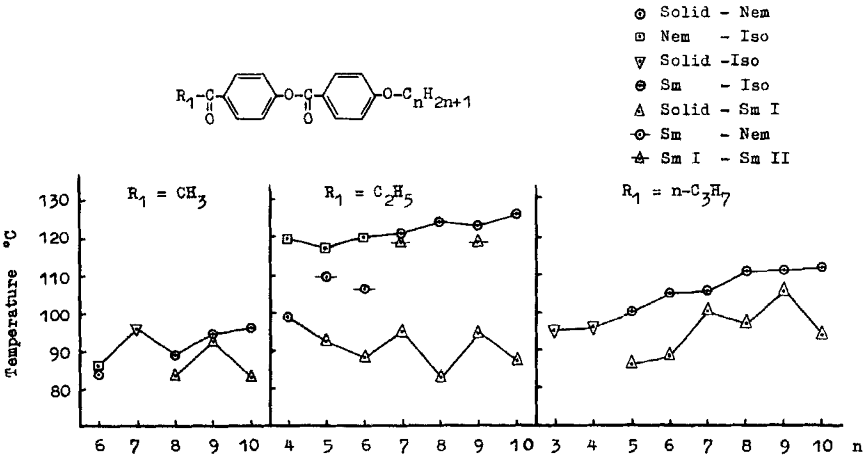


FIGURE 1 Phase transition plots for the *p*-acylphenyl esters of *p*-*n*-alkoxybenzoic acids.

The phase transition temperature has a regular alternation in accordance with the even or odd total number of atoms in both acyl and alkoxy chain. The melting points are more strongly affected by alternation in the alkoxy chain, and the clearing points show more marked jumps as the number of atoms in the acyl chain is changed.

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† The first figure (in the two-digit number) shows the number of carbon atoms in the keto chain; the second is the number of carbon atoms in the alkoxy chain.

2 DISCUSSION

The p-R-phenyl esters of p-n-alkoxybenzoic acids known at present form a nematic liquid crystal (where R = alk—O—, alk—COO— or alk—O—COO—).[2] The probability of appearance of a smectic modification for these compounds is likely to increase as the terminal chains become longer, i.e., when the lateral interaction dominates. The existence of a smectic modification in p-acylphenyl esters having short substituents is due to significant contribution of lateral interaction caused by presence of the keto group I in the molecule.

In acylphenyl esters there is conjugation between the carbonyl I and unshared electron pairs of the carboxyl oxygen *via* the π-benzene ring system and also conjugation between the carbonyl II and the unshared electron pairs of the alkoxy chain's oxygen (this type of conjugation also being in p-R-phenyl esters). It is evident that conjugation between the carbonyl group I and the π-benzene ring system leads to an increase in polarizability of this part of the molecule and to an increase in the dipole moment of the carbonyl due to the growth of partial negative charge on its oxygen. As a result there is an increase in the energy of intermolecular interactions of the dipole–dipole and dispersion types. This additional contribution to the energy of interaction between molecules predominates in the lateral direction and promotes the primary formation of a smectic mesophase starting with the lower homologues.

3 EXPERIMENTAL

p-n-Alkoxybenzoic acids were purified by recrystallization from glacial acetic acid.

p-Hydroxyacetophenone was purified by recrystallization from benzene. p-Hydroxypropiophenone and p-hydroxybutyrophenone were prepared by a Fries regrouping of the corresponding phenylpropionate and phenylbutyrate in a solution of nitrobenzene.[3] The products were purified chromatographically on Al_2O_3 with subsequent recrystallization from a 1:1 mixture of petroleum ether and ether.

p-Acylphenyl esters of p-n-alkoxybenzoic acids were prepared by reacting equimolecular quantities of p-hydroxyalkylphenone and p-n-alkoxybenzoic acid chloride in a current of nitrogen until no more HCl was given off. The products were purified chromatographically on Al_2O_3 (10 g of Al_2O_3 to 1 g acylphenyl ester) with subsequent recrystallization from cyclohexane or methanol. Satisfactory elemental analysis were obtained for all new compounds. The compounds and transition temperatures are recorded in Table I.

TABLE I

Transition temperatures for the *p*-acylphenyl esters of *p*-*n*-alkoxybenzoic acids

Compound R_1	R_2	Smectic I	Smectic II	Nematic	Isotropic
1	6	69[a]	—	84	86
1	7	67[a]	—	—	96
1	8	83.5	—	—	89
1	9	92.5	—	—	94
1	10	83	—	—	96
2	4	85[a]	—	99	120
2	5	92.5	—	110	117.5
2	6	88	—	116.5	120
2	7	95	119	—	121
2	8	83	—	—	124
2	9	94.5	119	—	123
2	10	87	—	—	126
3	3	—	—	—	95
3	4	94.5[a]	—	95.5[a]	96
3	5	86	—	—	100
3	6	88	—	—	105
3	7	100	—	—	105.5
3	8	97	—	—	111
3	9	105.5	—	—	111
3	10	94	—	—	112

[a] Indicate monotropy

Phase transitions and liquid crystal modification were fixed using an MNH-8 polarizing microscope equipped with a heating stage. Heating and cooling of the samples were carried out at the rate of 1° per minute.

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