SYNTHESIS AND LIQUID CRYSTALLINE PROPERTIES OF 2-SUBSTITUTED (5-PYRIMIDINYL) BENZOATES AND BENZOYLOXYBENZOATES

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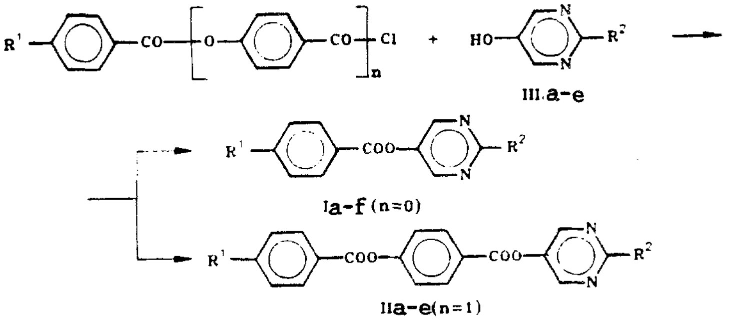
2-Substituted (5-pyrimidinyl) benzoates and benzoyloxybenzoates have been synthesized and their liquid crystalline properties have been studied. In general, these compounds exhibit a characteristic tendency to form a smectic mesophase.

The use of heteroaromatic fragments in place of aromatic substituents for the preparation of compounds with reduces viscosity and improved mesomorphic and physical properties appears to be a popular and common trand recently in the chemistry of liquid crystals. In addition to substituted arylpyridines [1], -pyridazines [2], -pyrazines [3], and especially -pyrimidines [4, 5], their ester derivatives have also been widely studied [6-10]; the latter are of interest as components in mixtures due to their low melting points [10].

Among the various ester derivatives of pyrimidinyl phenols the most widely studied members have been 2-(p-hyroxyphenyl)pyrimidine derivatives [10, 11]; data are also available concerning the liquid crystalline properties of 5-(p-hydroxyphenyl)pyrimidinyl carboxylates [12]. Recently 2-aryl-5-alkylcarbonyloxypyrimidines have also been reported to form stable, low-melting liquid crystals exhibiting a smectic C phase [4].

Continuing our studies of liquid crystalline arylpyrimidinyl carboxylates, which are nematic liquid crystals with a wide mesomorphic (mesophase) range [13, 14], and based on our recently discovered simple and convenient method for the preparation of 2-substituted 5-hydroxypyrimidines [15], we have synthesized the corresponding 5-pyrimidiyl benzoates I and benzoyloxybenzoates II and have studied their mesomorphic behavior relative to their isomeric pyrimidinyl esters and aromatic analogs.

Compounds I and II were prepared by reacton of the corresponding p-substituted benzoic acid chlorides with 2-substituted 5-hyroxypyrimidines (III) in pyridine [16].



I a-e, II a-e $R^1 = -OC_6H_{13}$; If $R^1 = -C_6H_{13}$; Ia—IIIa $R^2 = -C_6H_4Br\text{-}p$; Ib—IIIb, If $R^2 =$
$= -C_6H_4NO_2\text{-}p$; I—III c $R^2 = -C_6H_4OC_4H_9\text{-}p$, d $R^2 = -C_6H_4C_6H_{13}\text{-}p$, e $R^2 = SCH_3$

All these newly prepared compounds I and II, with the exception ofmonoester Ie, exhibited liquid crystalline properties. Using the binuclear compound Ie as an example, in analogy with the previously studied corresponding isomeric pyrimidine-2-carbonylic acid ester derivatives [17], we have found that replacement of either of the benzene rings in binuclear arylbenzoates [18, 19] by a pyrimidine ring leads to a loss or reduction in their mesomorphic properties. Chain elongation, i.e., conversion to a trinuclear diester such as IIe, leads, as expected [17, 18], to renewed mesomorphism; these compounds exhibit primarily smectic properties over a wide temperature range.

In contrast to their structural isomers, namely pyrimidine-containing carboxylic acid esters [13, 14], as well as 2-pyrimidinyl and (2-pyrimidinylphenyl) benzoates [18], the group of compounds above exhibit, in general, characteristic smectic properties. However, the presence of an electron-withdrawing (acceptor) end group, such as —Br or —NO_2, leads to nematic compounds exclusively, with notably broad mesophase (temperature) ranges for the latter. Nitro derivatives Ib, f represent an exception in this series of ester derivatives; they exhibit broad smectic and narrow nematic

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TABLE 1. Physical Characteristics of Esters Ia-f, IIa-e

Compound	Empirical formula	Recrystallization solvent	Phase transition temperatures*			ΔT, °C**	Yield, %
			T_s	T_n	T_i		
Ia	$C_{23}H_{23}BrN_2O_3$	Methanol	—	100	156	56	93
Ib	$C_{23}H_{23}N_3O_5$	Ethyl cellosolve	130	251	252	122	95
Ic	$C_{27}H_{32}N_2O_4$	Alcohol	97	155	219	122	89
Id	$C_{29}H_{36}N_2O_3$	Alcohol	76	175	189	113	83
Ie	$C_{16}H_{22}N_2O_3S$	Alcohol	—	—	76...77	—	93
If	$C_{23}H_{23}N_3O_4$	Acetone	132	215	219	87	93
IIa	$C_{30}H_{27}BrN_2O_5$	Pentane	—	135	245	110	80
IIb	$C_{30}H_{27}N_3O_7$	Methanol	—	138	299	161	87
IIc	$C_{34}H_{36}N_2O_6$	Ethyl acetate: Acetone, 1:1	94	287	304	210	88
IId	$C_{36}H_{40}N_2O_5$	Methylcellusolve, Acetone	80	219	259	179	95
IIe	$C_{25}H_{26}N_2O_5S$	Hexane	105	210	211	106	71

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*The phase transition temperatures refer to the smectic (T_s), nematic (T_n), and isotropic (T_i) phases.

**Mesomorphic temperature range.

mesophases. Aromatic analogs of our nematic bromo derivative Ia, in contrast, exhibit characteristic smectic mesomorphism [20]. Ester Ic also exhibits a wide nameatic mesophase along with broad smectic mesomorphism; compounds Ib-d and IIc, d exhibit in general smectic polymorphism, which can be observed visually in polarized light.

Alkyl-, alkoxy-, and dialkoxy terminally substituted esters Id, IId (~80°C) and Ic, IIc (~90°C), respectively, are characterized by the lowest mesophase transition temperatures (<100°C). The most thermally stable mesophase (~300°C) is formed by diesters IIb, c, although these differ greatly from one another in the nature of the terminal substituent attached to the pyrimidine fragment (NO_2 and C_4H_9O, respectively). Diester IIc, which has a relatively low melting point, also exhibits the widest temperature range for its mesomorphic state (~200°C).

EXPERIMENTAL

IR spectra were recorded on a UR-20 spectrophotometer using KBr pellets. Phase transition temperatures and mesophase structures or patterns were determined using a small-scale Boetius-type heating stage with a visual RNMK-0.5 accessory apparatus.

The 2-substituted 5-hydroxypyrimidine starting materials IIIa-e were prepared according to a literature procedure [15]. 2-(p-Butoxyphenyl)-5-hydroxypyrimidine (IIIc) was purified by recrystallization from a 1:2 mixture of chloroform—petroleum ether; mp 169-171°C.

2-Substituted 5-Pyrimidinyl Benzoates (Ia-f). A mixture of 2 mmoles p-hexyloxy- or p-hexylbenzoic acid (for esters Ia-e and ester If, respectively), 5 ml $SOCl_2$, and 10 ml absolute benzene was refluxed for 6 h, the benzene and excess $SOCl_2$ were evaporated under aspirator vacuum, and the residue was dissolved in 10 ml absolute benzene and again evaporated. The resulting acid chloride was then dissolved in 15 ml dry pyridine, 2 mmoles of the appropriate 5-hydroxypyrimidine IIIa-e was added, and the mixture was stirred for 2 days at 20°C. The reaction mixture was poured into 100 ml of 3 N HCl with ice. The precipitate was separated by filtration, washed with water (2 x 30 ml), and dried and recrystallized

2-Substituted (5-Pyrimidinyl) p-Hexyloxyphenylcarbonyloxybenzoates (IIa-e). A mixture of 3.5 mmoles p-hexyloxygenzoic acid, 5 ml $SOCl_2$, and 10 ml absolute benzene was refluxed for 6 h; the benzene and excess $SOCl_2$ were evaporated at aspirator pressure and the residue was dissolved in 15 ml anhydrous benzene and again evaporated to dryness. The resulting acid chloride derivative was dissolved in 15 ml dry pyridine, 3.5 mmoles p-hydroxybenzoic acid was added, and the mixture was stirred for 3 days at 20°C. The reaction mixture was poured into 100 ml 3 N HCl with ice. The precipitate was separated by filtration, washed with water (3 x 30 ml), and dried to give 3 mmoles (86%) of p-hexyloxybenzoic acid p-carboxyphenyl ester. IR spectrum: 1695, 1740 cm^{-1}. The nematic mesophase interval was 195-208°C. The ester was treated with 5 ml $SOCl_2$ in 10 ml anhydrous benzene, refluxed for 6 h, and subjected to the standard workup procedure to give the acid chloride derivative of p-(p-hexyloxybenzoyloxy)benzoic acid. The latter was dissolved in 15 ml dry pyridine and 3 mmoles of the appropriate 5-hydroxypyrimidine IIIa-e was added; the mixture was stirred for 2 days at 20°C and then poured into 150 ml of 3 N HCl in ice. The precipitate was separated by filtration, washed with water (3 x 30 ml), dried, and recrystallized.

The physical properties of these newly synthesized compounds are summarized in Table 1.

LITERATURE CITED

1. M. P. Burrow, G. W. Gray, D. Lacey, and K. Toyne, *Liq. Cryst.*, **3**, 1643 (1988).
2. J. C. Liang and J. O. Cross, *Mol. Cryst. Liquid. Cryst.*, **141**, 25 (1986).
3. M. Matsumoto, Y. Sonda, M. Ogasawara, T. Nagaishi, S. Yoshinaga, K. Isomura, and H. Taniguchi, *Chem. Express.*, **2**, 109 (1987); *Chem. Abstr.*, **108**, 104,337 (1988).
4. T. Sakurai, T. Yokota, E. Komatsu, N. Mikami, R. Higuchi, and K. Takeuchi, Eur. Patent Appl. 260,077 (EP); *Chem. Abstr.*, **109**, 201,674 (1988).
5. M. Sasaki, H. Takatsu, and K. Takeuchi, Kokai Tokkyo Kho 62,192,368 (Jpn.), *Chem. Abs*tr., **109**, 160,731 (1988).
6. A. Isenberg and H. Zaschke, *Z. Chem.*, **23**, 296 (1983).
7. G. W. Gray, K. Toyne, D. Lacey, M. R. Burrow, R. Eidenschink, A. Waechtler, and G. Weber, Ger. Offen. 3,600,052 (DE); *Chem. Abstr.*, **107**, 246,820 (1987).
8. R. Hopf, B. Scheuble, A. Waechtler, R. Hittich, R. Eidenschink, T. Geelhaar, J. Krause, and V. Reiffenrath, PCT Int. Appl. 87 0.1.717 WO; *Chem. Abstr.*, **107**, 49,772 (1987).
9. D. Demus, H. Zaschke, R. Paschke, and A. Wiegelben, Ger. Offen. 3,510,735 (DE); *Chem. Abstr.*, **104**, 79,323 (1986).
10. K. D. Scherf, H. Altmann, and H. Zaschke, Proc. 6th Liquid Crystal Conference Soc. Countr., Halle (1985), A-19.
11. S. M. Kelly and A. Villiger, *Liq. Cryst.*, **3**, 1173 (1988).
12. A. Murayama, S. Matsumoto, S. Takeno, and S. Sugita, Kokai Tokkyo Koho 63,230,674 (Jpn.); *Chem. Abstr.*, **110**, 125,654 (1989).
13. M. A. Mikhaleva, G. A. Kolesnichenko, K. I. Rubina, Yu. Sh. Gol'dberg, V. A. Savel'eva, L. Ya. Leitis, M. V. Shimanskaya, and V. P. Mamaev, *Khim. Geterotsikl. Soedin.*, No. 3, 380 (1986).
14. M. A. Mikhaleva, G. A. Kolesnichenko, T. A. Kizner, and V. P. Mamaev, *Khim. Geterotsikl. Soedin.*, No. 12, 1636 (1988).
15. T. A. Kizner, M. A. Mikhaleva, and E. S. Serbryakova, *Khim. Geterotsikl. Soedin.*, No. 6, 801 (1990).
16. S. Patai (ed.), *Them. Chemistry of Functional Groups. A. The Chemistry of Double-Bond Functional Groups,* Interscience, New York—London (1977), p. 112.
17. M. A. Mikhaleva, V. A. Savel'ev, A. I. Pavlyuchenko, M. F. Grebenkin, and V. P. Mamaev, *Khim. Geterotsikl. Soedin.*, No. 9, 1228 (1986).
18. D. Demus and H. Zaschke, *Synopsis of Tables of Liquid Crystals, II,* VEB Deutscher Verlag for Grundstofindustrie, Leipzig (1984), p. 230.
19. Kokai Tokkyo Koho 48-198,463 (Jpn.); *Chem. Abstr.*, **100**, 138,766 (1984).
20. J. C. Ducois and F. Barre, Ger. Offen., 2,600,588 (DE); *Chem. Abstr.*, **85**, 134,506 (1976).