LIQUID-CRYSTAL ω-(2-PYRIDYL)ACETOPHENONES AS REPRESENTATIVES OF MESOGENIC COMPOUNDS WITH AN INTRAMOLECULAR HYDROGEN BOND

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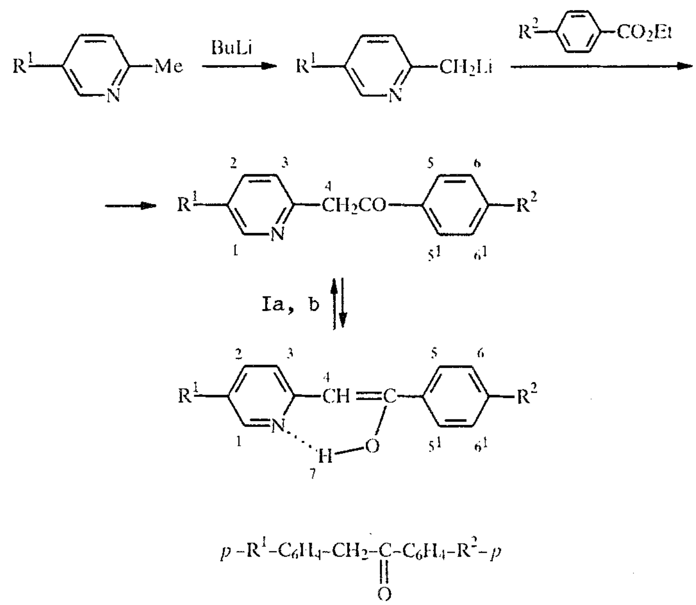
Representatives of a new class of mesogenic compounds have been synthesized, ω-(5-substituted-2-pyridyl)-4-alkylacetophenones, which have an intramolecular hydrogen bond. The mesogenic properties of these compounds have been investigated.

Continuing our studies of the influence of a hydrogen bond on mesogenic properties [1, 2], we have synthesized ω-(5-substituted-2-pyridyl)-4-alkylacetophenones (I) and have compared their mesogenicity with that of their benzene analogs (II).



II

Ia $R^1 = C_6H_{13}$, $R^2 = OC_7H_{15}$; Ib $R^1 = C_6H_{13}$, $R^2 = C_7H_{15}$

Our initial premise was that compounds containing a CH_2CO fragment can exist in keto and enol forms; but, in contrast to the phenylacetophenone II, the pyridylacetophenone I in the form of the enol tautomer will have an intramolecular hydrogen bond (IHB) [3, 4].

The p-substituted phenacylpyridines Ia and Ib that we obtained do have mesogenic properties, whereas their benzene analogs II do not have a mesophase (Table 1). Compounds Ia and Ib also differ from II in that they have a hydrogen bond, as indicated by their PMR spectra.

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TABLE 1. Mesogenicity of Synthesized Compounds

Compound	R^1	R^2	Phase transition temperature*	ΔT, °C
Ia	C_6H_{13}	OC_7H_{15}	C 48 S_2 55 S_1 65,5 I	17,5
Ib	C_6H_{13}	C_7H_{15}	C 30 Sa 70,2 I	40,2
II	C_6H_{13}	C_7H_{15}	C 59 I	—

*C = crystal; S = smectic phase; I = isotropic melt; Δ = width of temperature interval of existence of mesophase.

TABLE 2. IR Spectroscopic Data on Synthesized p-Substituted Phenacylpyridines

Compound	R^1	R^2	In KCl tablets		In CCl_4	
			$\nu_{C=O}$, cm^{-1}	$\nu_{C=C}$ cm^{-1}	$\nu_{C=O}$ cm^{-1}	$\nu_{C=C}$, cm^{-1}
Ia	C_6H_{13}	OC_7H_{15}	—	1629	1667	1627
Ib	C_6H_{13}	C_7H_{15}	—	1624	1669	1623

TABLE 3. PMR Spectroscopic Data on Synthesized Compounds (spectra taken in $CDCl_3$ at T = 303 K)

Compound	Chemical shifts of protons δ, ppm						Form, %
	1-H	2-H	3-H	4-H	5,5'-H	6,6'-H	
Ia	8,38	7,45	7,22	4,41 5,97*	8,05	6,91	Ketone, 90 Enol, 10
Ia +**	8,36	7,44	7,18	4,45 5,92*	8,03	6,92	Ketone, 60 Enol, 40
Ib	8,38	7,45	7,21	4,44 6,03*	7,99	7,25	Ketone, 76 Enol, 24
II	7,15	7,15	7,17	4,23	7,95	7,26	Ketone, 100

*Signal of protons of enol OH group is not observed in the spectrum, probably as a result of strong broadening.

**Ia^+: Spectrum taken at T = 385 K in an isotropic melt in a coaxial capillary.

Such a difference in mesogeneity of the synthesized compounds is apparently related to the formation of an additional ring through an IHB, which corresponds to increasing the polarizability of the molecules of Ia and Ib. These same factors make the molecules more prone to mesophase formation.

As shown by IR spectroscopic data, the p-substituted phenacylpyridines in the solid state exist in the enol form (the frequency of carbonyl group stretching vibrations is absent); but in CCl_4 solution, the keto form appears (frequency of C=O stretching vibrations is in the 1667-1669 region (Table 2).

In the PMR spectrum of compound Ia in an isotropic melt, a mixture of the keto and enol forms is observed, with the keto form predominating (60%).

It was established by PMR spectroscopy that compound Ia in $CDCl_3$ solution at room temperature consists of 90% keto form and 10% enol; under these same conditions, compound Ib consists of 76% keto form and 24% enol (Table 3).

Indirect evidence for the presence of an IHB and a mobile proton may be found in the luminescence of the p-substituted phenacylpyridines I in the yellow-green region.

EXPERIMENTAL

The IR spectra were recorded in a Perkin-Elmer instrument in KCl tablets or in CCl_4 solution. The PMR spectra were recorded in a Bruker WP-80CW instrument in $CDCl_3$. The purity of the compounds was monitored by TLC.

Elemental analyses were in agreement with calculated values. The phase transition temperatures were measured on a Boethius heated stage (NMK) with polaroid films.

The compounds I were synthesized through organolithium compounds by means of a scheme that is described in [5, 6]. The analog II was synthesized by Friedel—Crafts acylation of an alkylbenzene by the appropriate phenacyl chloride in the presence of $AlCl_3$ [7, 8], yield 8%. The original 2-methyl-5-hexylpyridine was obtained from 6-methylnicotinic acid by a method given in [9]. The ethyl esters of p-heptyloxy- and p-heptylbenzoic acids were obtained from the corresponding acids by esterification with ethanol in the presence of H_2SO_4, by analogy with data reported in [10].

Substituted ω-(2-Pyridyl)acetophenones (Ia,b). To 20 ml of anhydrous ether in a nitrogen atmosphere at −30°C, 15 ml (0.0141 mole) of a 6.4% solution of butyllithium in hexane was added. To this mixture, at the same temperature, with vigorous stirring, 2 g (0.0124 mole) of 2-methyl-5-hexylpyridine in 10 ml of absolute ether was added dropwise. The mixture was stirred for 30 min more at this same temperature, after which 0.0124 mole of the appropriate ethyl ester of a p-substituted benzoic acid was added. Stirring was continued for 1 h; the mixture was allowed to warm to room temperature, heated to boiling, refluxed for 30 min, and again cooled to room temperature, after which 3 ml of water was added and the mixture was poured onto 25 g of crushed ice and 4 ml of 6 N HCl. The ether layer was separated off, and the aqueous layer was neutralized to pH 6-7 and extracted three times with ether. The combined ether extracts were dried with Na_2SO_4, the solvent was driven off, and the residue was chromatographed in a column (d 40 mm, h 120 mm) with silica gel 5/40 μm, in benzene. A yellow substance was obtained after crystallization from ethanol. Yield of compound Ia 4%, Ib 5%.

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