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MESOMORPHIC PROPERTIES OF N-(4-ETHYLPYRIDINIO)-4-ALKOXYBENZAMIDATES: YLIDE AS A LIQUID CRYSTAL

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N-(4-Ethylpyridinio)-4-alkoxybenzamidates (1) were prepared and their phase transition properties were determined. The ylides with long alkoxyl groups (1, n=4-8) exhibit liquid crystallinity, while methoxy, ethoxy, and propoxy homologs are not mesomorphic.

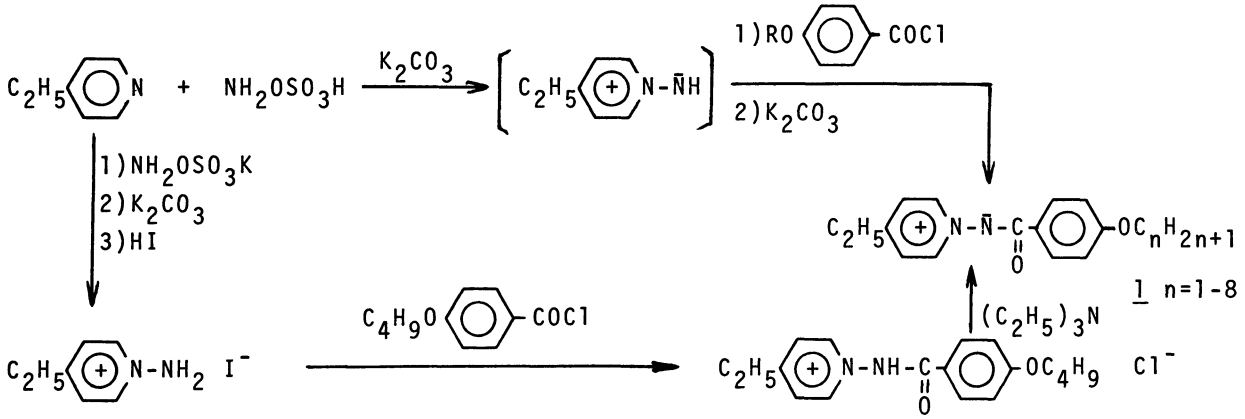
It is known that most nematic and smectic liquid crystals are rod-like molecules with both rigid aromatic moieties and easily polarizable groups which are essential for the anisotropic interactions between the induced dipole moments of the molecules. These structural characteristics of liquid crystalline compounds and the similarity of electronic structure of nitrogen ylides to that of azoxy compounds which often exhibit liquid crystallinity led us to the examination of the phase transition of pyridinium ylides. This letter describes preparation and mesomorphic properties of N-(4-ethylpyridinio)-4-alkoxybenzamidates (1).

The mixture of hydroxylamine O-sulfonic acid with two equivalents of 4-ethylpyridine in water-methanol was heated at 80 °C for 2.5 h. After neutralization with potassium carbonate, the solvents were evaporated under reduced pressure, and the organic matters were extracted with ethanol. 4-Alkoxybenzoyl chloride was added to the ethanol solution, and after 2 h reaction at room temperature, potassium carbonate was added. The precipitates were filtered off, and the solvent was evaporated. Extraction with and evaporation of ether gave crude product which was purified by recrystallization three times from ethanol-hexane (Scheme 1).

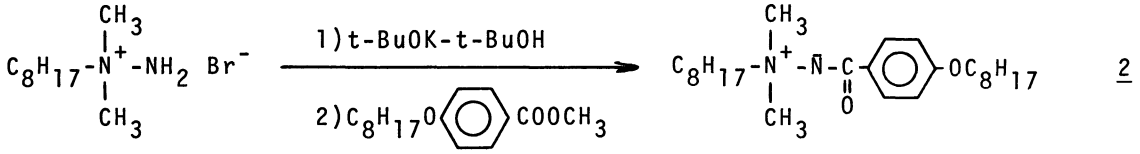
Alternatively, N-(4-butoxybenzoylamino)-4-ethylpyridinium chloride (hydrochloric acid salt of 1, n=4) was prepared by the reaction of N-amino-4-ethylpyridinium iodide (prepared by the modified method of Gösl)[1] with 4-butoxybenzoyl

chloride. The pyridinium chloride was then treated with triethylamine in dichloromethane to afford 1 (n=4) (Scheme 1). The two synthetic methods gave thermally and spectroscopically identical products.

N-(Dimethyloctylammonio)-4-octyloxybenzamidate (2) was prepared by the reaction of 1,1-dimethyl-1-octylhydrazinium bromide with methyl 4-octyloxybenzoate in t-butyl alcohol in the presence of potassium t-butoxide [2,3] (Scheme 2). The structures of the aminimides were confirmed with IR, NMR, and MS, and their purity was checked by elemental analyses. Transition temperatures were determined with a differential scanning calorimeter and also with a capillary tube melting point apparatus.



Scheme 1



Scheme 2

The experimental data are summarized in Table 1. Methoxy, ethoxy, and n-propoxy derivatives (1, n=1,2, and 3) are not mesomorphic, while higher alkoxy derivatives (1, n=4-8) exhibited mesomorphism. The mesophase-isotropic phase transition temperature increases with the length of the alkoxyl groups, although no definite tendency is found for crystal-mesophase transition temperature. n-Butoxy derivative showed two mesophases, while higher alkoxy derivatives have single mesophase. These were tentatively assigned to be smectic, since all of the thermotropically liquid crystalline soaps including pyridinium halides and 4-alkoxyaniline hydrochlorides that have been reported are smectic rather than

Table 1. Properties of aminimides (1 and 2)

n in 1	$\nu_{C=O}$ (cm^{-1})	Transition	temp. (°C)*	ΔH_t (kJ mol^{-1})	ΔS_t (J $mol^{-1}K^{-1}$)
1	1595	C-I	146	25.0	59.8
2	1599	C-I	185	32.0	70.2
3	1598	C-I	172	29.8	66.8
4	1597	C-S	150	27.2	64.4
		S-S'	155	0.712	1.66
		S'-I	158	0.787	1.82
5	1597	C-S	111	25.0	65.0
		S-I	159	3.10	7.15
6	1595	C-S	123	21.9	55.3
		S-I	175	3.28	7.34
7	1595	C-S	126	22.4	56.1
		S-I	179	4.23	9.38
8	1594	C-S	120	20.6	52.7
		S-I	183	3.80	8.34
2	1598	C-I	74	17.4	50.3

* C=Crystal, S=Smectic, I=Isotropic.

nematic.[4] One of the mesophases of n-butoxy compound at 155-158 °C can be nematic. N-(Dimethyloctylammonio)-4-octyloxybenzamidate (2) is not mesomorphic, which seems to indicate that molecular planarity or enhanced polarizability by pyridine ring is essential for mesomorphism.

Several ammonium compounds have been known to display thermotropic mesomorphism. Examples are alkylpyridinium halides,[5] 2-alkylpyridine hydrochlorides,[5] 4-alkoxybenzamidine hydrochlorides,[6] and 4-alkoxyaniline hydrochlorides.[4] Aminimides with long hydrocarbon chains are known to exhibit surface activity and form lyotropic liquid crystalline phases,[7,8] but, to our best knowledge, thermotropic mesomorphism of aminimides as well as other ylide compounds has not been reported yet.

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