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LIQUID CRYSTALLINE PROPERTIES OF LATERALLY SUBSTITUTED BENZYLIDENEANILINE DERIVATIVES

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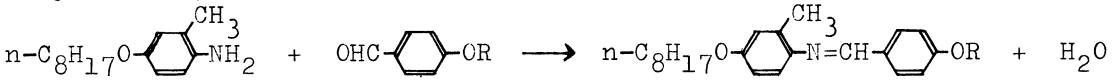
A new series of anils, N-(p-alkoxybenzylidene)-2-methyl-4-octyloxyanilines, has been synthesized and investigated for the liquid crystalline property. These compounds exhibit nematic behavior in relatively low temperature range and make a well known change of nematic-isotropic transition temperatures. No smectic phase appears even in the case of longer chain derivatives.

Many workers have been interested in liquid crystals since the application of their new electro-optic effect to display devices was presented[1]. A great number of p,p'-dialkoxybenzylideneanilines are known to exhibit nematic and/or smectic behavior[2,3], the high nematic temperature range restricts the application to practical devices. In this study, it is our purpose to investigate the effect of an additional lateral methyl substitution to these compounds on mesomorphic properties.

N-(p-alkoxybenzylidene)-2-methyl-4-octyloxyanilines (I) were prepared by the usual condensation of 2-methyl-4-octyloxyaniline (II) with p-n-alkoxybenzaldehydes (III):

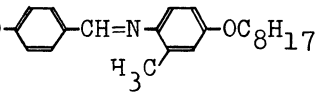


(II) (III) (I)

(R = CH_3, C_2H_5, ..., n-C_8H_{17})

After 33g of 1-nitro-2-methyl-4-n-octyloxybenzene (IV, bp 176.0-176.5°C/2mmHg) was prepared by refluxing a solution of 28g of 3-methyl-4-nitrophenol, 15g of potassium hydroxide and 39g of n-octyl bromide in 200ml of alcohol, the reduction of the compound IV using stannous chloride and hydrochloric acid gave a nearly quantitative yield of the compound II (bp 149-152°C/2mmHg). p-n-Alkoxybenzaldehydes, with the exceptions of commercially availlable p-anisaldehyde and p-ethoxybenzaldehyde, were prepared by method of Stoermer and Wodarg[4]. Condensation of about 3g of the compound II and the equimolar quantities of the appropriate compound III was carried out in ethanol at 50°C. Crystalline products were obtained in 50-80% yields after recrystallization.

The observed transition temperature and the analytical data of the synthesized anils are shown in Table 1. It is a remarkable result that all of the compounds exhibit only the nematic mesophase in the temperature range much lower than p,p'-dialkoxybenzylideneanilines[2,3], and yet no smectic mesophase

Table 1. Synthesized Anils, RO-  -OC$_8$H$_{17}$

R	Elemental Analysis, C% Found	C% Calcd.	H% Found	H% Calcd.	N% Found	N% Calcd.	Temp. (°C) of Transition* from C. to N.	from C. or N. to I.	from I. to N.	from N. to C.
CH_3	78.07	78.15	8.56	8.84	3.99	3.96	—	54.5	53.0	47.0
C_2H_5	78.53	78.43	8.87	9.05	3.70	3.81	63.5	71.0	71.0	43.5
n-C_3H_7	79.00	78.70	9.19	9.25	3.60	3.67	45.7	57.5	57.8	24.8
n-C_4H_9	79.37	78.93	9.53	9.43	3.53	3.54	50.3	67.2	67.3	<25
n-C_5H_{11}	——— not analyzed ———						—	62.5	61.4	43.5
n-C_6H_{13}	79.72	79.39	9.83	9.76	3.42	3.31	54.5	64.5	64.5	41.5
n-C_7H_{15}	79.72	79.73	9.93	9.90	3.28	3.20	—	63.0	63.0	52.0
n-C_8H_{17}	80.05	79.77	10.21	10.04	3.27	3.10	48.0	64.5	64.6	<25

* C., N. and I. denote crystalline, nematic and isotropic states respectively.

appears even in the case of long chain derivatives. On the other hand, the compounds show behaviors commonly seen in the other mesomorphic compounds containing p-alkyl or -alkoxy groups[5,6]. When the chain length of the p-substituents is defined as the number of the carbon and the oxygen atoms, the homologous members containing odd-numbered substituents exhibit higher nematic-isotropic transition temperatures than those containing even-numbered substituents.

It is presumable from these facts that the lateral methyl substituent decreases the lateral intermolecular cohesion and has no important effect upon the terminal intermolecular cohesion.

The reactivity of the anils to tartaric acid in ethanol solution was measured to determine the chemical stability by using -CH=N- absorption band at 320-325 mμ. It was found that the absorption of the anil with a lateral methyl substituent decreased about ten times slower than that of the anil without. This fact may indicate that the lateral methyl substituent stabilizes -CH=N- bond structurally.

Finally, electro-optic effects of these new compounds were observed. Because of the high contrast ratio and the chemical stability which results in the long service life, the compounds can be used for display elements.

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