bands are assigned at about 1620 cm^{-1} and 920 cm^{-1}, respectively.

In the ultraviolet region there is a characteristic intense band at about 250 mμ which is assigned as benzene band II (*2*). This band is discriminated by its position an magnitude of intensity. Substitution of R_2 by a naphthalene ring results in greater bathochromic shift and the bands observed at 225 and 270 mμ are the naphthalene bands I and II, respectively. The assignment of these bands are supported by comparing the spectra of *N*-arylhydroxamic acids with structurally related compounds (*7, 11*). In the hydroxamic acids derived from naphthoic acid, the ratio of bands II, and I, λ_{II}/λ_{I}, is generally found at about 1.22 (*3, 4*).

EXPERIMENTAL

Materials and Apparatus. Infrared spectra were recorded in the 2- to 15-μ region on a Perkin-Elmer Model 221 or Model 137 spectrophotometer equipped with sodium chloride optics and calibrated by standard methods. Solids were dried over P_2O_5 finely powdered in an agate mortar, and examined as KBr pellets or mulls in Nujol.

The ultraviolet absorption spectral measurements were recorded on a Hilger and Watts Model H 9998/62271 ratio recording spectrophotometer, with 10-mm matched stoppered quartz cells in the 200- to 350-mμ region.

Spectroscopic grade 95% ethyl alcohol, which was sufficiently transparent up to 200 mμ, was specially purified from ethanol.

Acid Chlorides. The acid chlorides were prepared by the action of thionyl chloride on the corresponding carboxylic acids and were vacuum distilled. The pure 2,4-dimethoxy benzoyl chloride is difficult to prepare, because it gives a dark violet color on addition of thionyl chloride to 2,4-dimethoxy benzoic acid. The pure white solid acid chloride was obtained after two to three distillations under vacuum. All the other acid chlorides except 2-naphthoyl chloride, which is a solid, were obtained as colorless liquids.

Preparations. All arylhydroxylamines were freshly prepared and crystallized two times from a mixture of benzene and petroleum ether.

A typical preparation of *N*-phenyl-2-naphthohydroxamic acid is given below.

10.9 Grams (0.1 mole) of *N*-phenylhydroxylamine was dissolved in 150 ml of cold diethyl ether, and the solution was stirred mechanically with external cooling to lower the temperature to 0° or below. Powdered sodium bicarbonate [12.6 grams (0.15 mole)] suspended in 15 ml of water were added to this solution. To this, 18.95 grams (0.95 mole) of the 2-naphthoyl chloride dissolved in 100 ml of diethyl ether were added dropwise during the course of 1 hr. The reaction mixture was always kept basic. Usually a yellowish white liquid was obtained, which was precipitated with petroleum ether at low temperature. The ether layer was removed under vacuum at room temperature. Any solid material thus obtained was combined with the bulk of the product which was thoroughly triturated in a porcelain mortar with an excess of saturated sodium bicarbonate solution to remove the acid impurities. The solution was filtered, and the solid was washed with water and dried. The product was crystallized from a mixture of benzene and petroleum ether. The yield of once crystallized product, mp 156°, was 70%.

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Synthesis and Transition Temperatures of *N*-(*p*-Alkoxybenzylidene)-*p*′-acyloxyanilines

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The discovery of the dynamic light scattering effect in certain nematic liquid crystals when subjected to an electrical field (*5*) has stimulated widespread interest in these compounds because of their potential application in flat panel displays (*4*). In searching for nematic liquid crystal systems (*6*) having favorable mesomorphic temperature ranges, we prepared an extensive series of *N*-(*p*-alkoxybenzylidene)-*p*′-acyloxyanilines (I). The synthesis and transition temperatures for these compounds are reported here.

Our synthetic approach involved the acylation of the corresponding *N*-(*p*-alkoxybenzylidene)-*p*′-hydroxyaniline (II)l Many of the reported acylation reactions (*7*) proved impractica.

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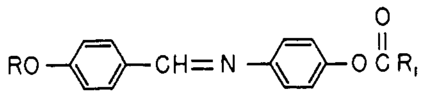
N-(p-Alkoxybenzylidene)-p'-acyloxyanilines can be prepared conveniently by the reaction in aqueous solution of the appropriate anhydride and the sodium salt of N-(p-alkoxybenzylidene)-p'-hydroxyaniline. Reaction temperatures, percent yields, melting points, and mesomorphic to isotropic transition temperatures are given for the reported compounds, all of which are nematic liquid crystals.

Table I. Physical Data of Benzylidene Esters (I)[a]

Compound no.	R[b]	R_1[b]	Acylation reaction time, min	Acylation reaction temp, °C	Yield, %	Mp, °C	Mesomorphic to isotropic transition temp, °C
1	CH_3	CH_3	15	25	74	83-4	109.0-109.5
2	CH_3	C_2H_5	15	30	68	64-5	114.0-114.5
3	CH_3	C_3H_7	15	40	73	50-1	112.5-113.0
4	CH_3	C_4H_9	15	50	62	58-9	98.5-99.0
5	CH_3	C_5H_{11}	20	60	60	81-2	101.5-102.0
6	CH_3	C_6H_{13}	25	60	61	63-4	96.5-97.0
7	C_2H_5	CH_3	15	25	75	109-10	132.0-132.5
8	C_2H_5	C_2H_5	15	30	71	111-12	136.0-136.5
9	C_2H_5	C_3H_7	15	40	66	97-8	135.0-135.5
10	C_2H_5	C_4H_9	15	50	62	84-5	123.0-123.5
11	C_2H_5	C_5H_{11}	20	60	63	71-2	124.0-124.5
12	C_2H_5	C_6H_{13}	25	60	60	63-4	116.5-117.0
13	C_3H_7	CH_3	15	25	73	94-5	105.0-105.5
14	C_3H_7	C_2H_5	15	30	70	97-8	112.5-113.0
15	C_3H_7	C_3H_7	15	40	68	74-5	112.3-112.5
16	C_3H_7	C_4H_9	15	50	65	68-9	103.2-103.5
17	C_3H_7	C_5H_{11}	20	60	61	83-4	107.2-107.5
18	C_3H_7	C_6H_{13}	25	60	63	71-2	100.4-100.8
19	C_4H_9	CH_3	15	25	77	80-1	110.5-111.0
20	C_4H_9	C_2H_5	15	30	74	84-5	117.5-118.0
21	C_4H_9	C_3H_7	15	40	66	86-7	119.5-120.0
22	C_4H_9	C_4H_9	20	50	71	76-7	112.5-113.0
23	C_4H_9	C_5H_{11}	25	60	63	80-1	115.0-115.5
24	C_4H_9	C_6H_{13}	30	60	60	72-3	109.5-110.0

[a] Elemental analyses for (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] All alkyl groups are n-isomers.

Table II. Physical Data of Benzylidene Phenols (II)[a]



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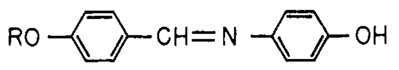

II

R	Yield, %	Mp, °C	Color
CH_3	73	188-9	Beige
C_2H_5	71	176-7	Yellow
n-C_3H_7	67	182-3	Light beige
n-C_4H_9	69	154-5	Yellow

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review.

because of hydrolysis of the esters (acid catalyzed reactions) or the tedious isolation required of products (pyridine catalyzed reactions).

The most favorable approach with respect to reaction time and yield was a modification of the Chattaway (*1*) procedure which required the addition of the appropriate anhydride to an aqueous solution of the sodium salt of II. With the exception of the reactions conducted with acetic anhydride, all reactions required heating because of the low solubility of the higher molecular weight anhydrides. Reaction temperatures are shown in Table I. The ratio of reactants was critical, and the optimum molar ratio was found to be II:NaOH:anhydride = 1:4:1.5. The excess NaOH inhibited hydrolysis of the anil. On cooling, only the desired product crystallized out leaving all other components in solution. One recrystallization was sufficient to obtain products of analytical purity.

The use of heat in acylation reactions on basic solutions of phenols is normally not recommended. However, the synthesis of the esters in Table I shows that the phenoxide ion can compete with the hydroxide ion in nucleophilic attack on the anhydride even under these conditions. Hydrolysis of the higher molecular weight esters does not occur to an appreciable degree even upon prolonged heating. This was shown by the preparation of N-(p-n-butoxybenzylidene)-p'-capryloxyaniline. Heating the reaction for 30 min at 30°C yielded 25% more product than heating 15 min. The resistance of the ester to saponification apparently stems from its near total insolubility even in hot water.

EXPERIMENTAL

Reagents p-anisaldehyde, p-ethoxybenzaldehyde, and p-aminophenol and all the anhydrides were purchased from the Aldrich Chemical Co. and used without further purification. p-n-Propoxybenzaldehyde and p-n-butoxybenzaldehyde were prepared according to the procedure of Covello and Piscopo (*2*).

Preparation of N-(p-methoxybenzylidene)-p'-hydroxy-

aniline. A solution of *p*-anisaldehyde (13.6 grams, 0.1 mole), *p*-aminophenol (11.0 grams, 0.1 mole), concentrated hydrochloric acid (5 ml), and 100 ml of 95% aqueous ethanol was refluxed for 1 hr. Upon cooling to −20°C, crystals formed and were removed by filtration. Recrystallization from a water–ethanol mixture yielded *N*-(*p*-methoxybenzylidene)-*p*′-hydroxyaniline, 16.7 grams, 73%, mp 188°. The other *N*-(*p*-alkoxybenzylidene)-*p*-hydroxyanilines were prepared using the same procedure. The data on these compounds are given in Table II.

Preparation of *N*-(*p*-methoxybenzylidene)-*p*′-butyryloxyaniline (III). To a solution of sodium hydroxide (1.6 grams, 0.4 mole) in 70 ml of water, *N*-(*p*-methoxybenzylidene)-*p*′-hydroxyaniline (2.3 grams, 0.1 mole) was added with stirring. The solution was heated to 50°C. *n*-Butyric anhydride (2.3 grams, 0.015 mole) was added, and stirring continued for 15 min. The solution was then placed in a freezer at −20°C for 1 hr and filtered, and the residue was washed with cold water. The crystals were then recrystallized from heptane. The yield of III was 1.6 grams, 60%, mp 58–9°C. The other esters were prepared using the above procedure. All the benzylidene esters formed were crystalline and white. The physical data are listed in Table I.

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