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Alkyl Carbonato Terminally Substituted Anils†

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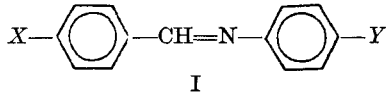
Abstract—Several types of p,p'-disubstituted anils containing an alkyl carbonato terminal substituent have been prepared. Numerous examples of these generally unknown anils, in which X in Formula I is alkyl carbonato and Y is alkoxy, acyloxy, alkyl keto, or alkyl carbonato, or with X and Y interchanged, have been synthesized.



I

Many are characterized by relatively low mesomorphic transition temperatures and intermediate mesomorphic temperature ranges.

The preparative methods for the individual classes of anils and tabulation of their mesomorphic temperature ranges are included along with a comparison of these data with corresponding data for anils not containing an alkyl carbonato terminal substituent.

1. Introduction

The realization that many nematic liquid crystalline materials under suitable electrical excitation exhibit dynamic scattering of light has provided the spark for much recent synthetic effort in the quest for new liquid crystals. The need for novel nematic liquid crystalline (mesomorphic) materials (or mixtures thereof) is important because:

1) room-temperature nematic materials are required for most electro-optical liquid-crystal devices,

2) only three compounds have been reported which are nematic at room temperature:

† Presented at the 4th International Liquid Crystal Conference, August, 1972, Kent, Ohio.

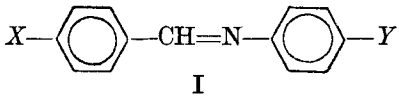
a) three *p,p'*-di-*n*-alkylazoxybenzenes[1a]
b) *trans*-*p*-(2-methylhexyl)-α-chloro-*p'*-ethoxystilbene[1b]
c) N-(*p*-methoxybenzylidene)-*p'*-*n*-butylaniline (MBBA)[2]
d) 2,4-nonadienoic acid[3]

3) within the anil (Schiff base) family of mesomorphic materials, MBBA appears to be relatively unstable and is often incompatible with other materials present in electro-optical devices, and

4) new room-temperature or near-room-temperature nematics may be more useful in devices than those materials presently employed if such characteristics as increased chemical stability and different dielectric anisotropies are available. A portion of the materials synthesis effort of our liquid crystal program includes the preparation of generally unreported anils, and this report is concerned with benzylidene anils containing one or more *p*-alkyl carbonato groups.

Schiff bases (anils, imines, or azomethines) have enjoyed thorough and continuous attention because a high percentage of *p,p'*-disubstituted benzylideneanilines are nematic and/or smectic mesomorphic materials. Much of the older literature has been compiled by Kast,[4] Gray[5] and others have empirically determined that nematic and smectic mesomorphic materials are usually long cigar- or rod-shaped molecules. The mesomorphic state of matter is intermediate between that of a crystalline solid and an isotropic liquid, and is promoted by a favorable balance between intermolecular lateral and terminal cohesive forces, which play a controlling role in the incidence and stability of the mesomorphic state. The intermolecular packing in the solid state affects the stability of the crystalline solid state with respect to formation of mesomorphic states. Properly *p,p'*-disubstituted Schiff bases as a class seem to fulfill these molecular requirements very well, and much of the knowledge of the phenomena of liquid crystals has been gained through studies of certain Schiff bases.

Mesomorphic materials within the Schiff base family can be represented schematically by I.



I

Some typical X and Y substitution patterns, within which are contained mesomorphic members, are listed below.

X	Y	Ref.
alkoxy	alkyl	2,6
alkyl	alkoxy	2,6
alkoxy	acyloxy	7,8
acyloxy	alkoxy	7
alkoxy	alkoxy	9
alkoxy	cyano	10
alkyl	cinnamoyl	11
alkoxy	cinnamoyl	11
alkoxy	ω-hydroxyalkyl	12
alkoxy	acyl	13

The R-group chain lengths within each of the above X and Y substituents are *nonbranched* alkyl groups, usually ten or less carbon atoms in length.

2. Results and Discussion

The anils discussed in this report have the general formula I, where X and/or Y are the n-alkyl carbonato group. The specific series of compounds and their tabular designation are as follows.

X	Y	Series	Table
alkoxy	carbonato	Ia	1
carbonato	alkoxy	Ib	2
acyloxy	carbonato	Ic	3
carbonato	acyloxy	Id	4
carbonato	acyl	Ie	5
carbonato	carbonato	If	6

This tabular survey of n-alkyl carbonato-substituted Schiff bases and their mesomorphic transitions is not intended to be exhaustive but rather representative. Some of the series were examined more extensively than others, depending upon the broadness of the nematic range and the proximity of the crystalline-to-nematic phase transition to room temperature.

Tables 1–6 demonstrate that no room-temperature, single-component nematic materials were obtained during this study. However, the importance of the synthetic study of these anils lies with the fact that certain trends relating to the position (proximity to room temperature) and breadth of the mesomorphic ranges of these compounds are evident and that new low-temperature nematic mixtures of these anils can be prepared.

Figure 1 shows a plot of the crystal-to-nematic (C → N) and nematic-to-isotropic (N → I) transition temperatures of the N-(*p*-pentyloxybenzylidene)-*p'*-alkoxycarbonyloxyanilines (Series Ia) as a function of the R-group chain length in substituent *Y* (Formula I). On this same graph are plotted the corresponding data for compounds of Series Ib, the N-(*p*-alkoxycarbonyloxybenzylidene)-*p'*-pentyloxyanilines. Three noteworthy patterns emerge. Firstly, the plots of N → I transition temperatures for each series assume a generally alternating pattern. Within each series a line joining the transition temperatures for members with even-numbered carbon chains lies

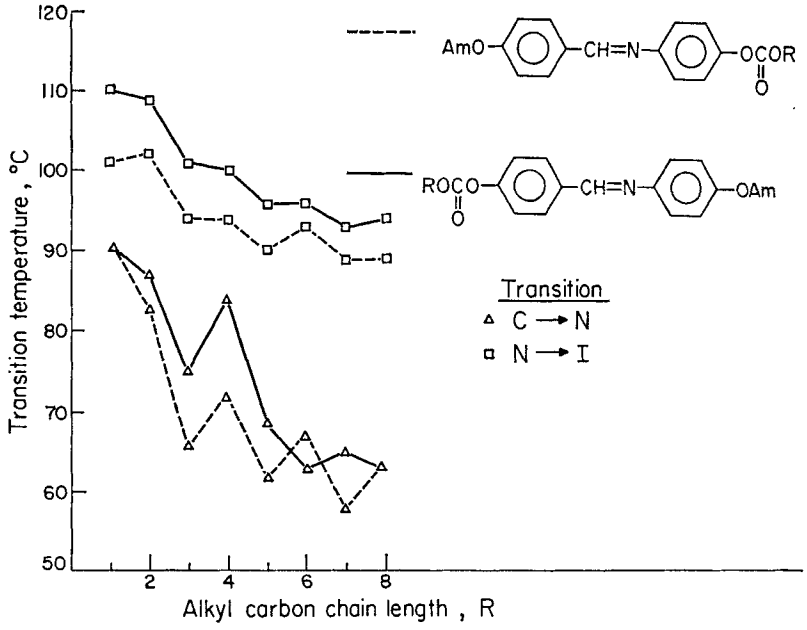
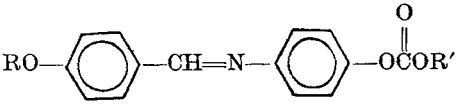


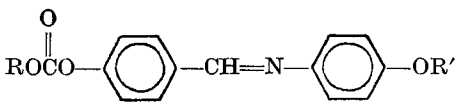
Figure 1. Transition temperatures for *p*-pentyloxy-*p'*-alkoxycarbonyloxy anils vs. *p*-alkoxycarbonyloxy-*p'*-pentyloxy anils.

TABLE 1 

No.	*n*-R	*n*-R′	Range (°C)[a]
1[b]	CH_3	CH_3	84–110
2[b]	CH_3	C_2H_5	81–103
3[b]	CH_3	C_3H_7	78– 90
4[b]	CH_3	C_4H_9	68– 84
5[b]	CH_3	C_5H_{11}	47– 81
6[b]	CH_3	C_6H_{13}	65– 74
7	CH_3	C_8H_{17}	76– 78
8[b]	C_2H_5	CH_3	87–128
9[b]	C_2H_5	C_2H_5	94–119
10	C_2H_5	C_3H_7	87–112
11	C_2H_5	C_4H_9	83–107
12	C_2H_5	i-C_4H_9	96– 98
13[b]	C_2H_5	C_5H_{11}	75–101
14[b]	C_2H_5	C_6H_{13}	78–103
15	C_3H_7	CH_3	100–108
16	C_3H_7	C_5H_{11}	59– 90
17[b]	C_4H_9	CH_3	69–115
18[b]	C_4H_9	C_2H_5	90–119
19[b]	C_4H_9	C_3H_7	79–106
20	C_4H_9	C_4H_9	68–100
21[b]	C_4H_9	C_5H_{11}	65–100
22[b]	C_4H_9	C_6H_{13}	56– 96
23[b]	C_4H_9	C_7H_{15}	69– 94
24	C_4H_9	C_8H_{17}	80– 93
25	C_5H_{11}	CH_3	91–105
26	C_5H_{11}	C_2H_5	83–104
27[b]	C_5H_{11}	C_3H_7	66– 94
28[b]	C_5H_{11}	C_4H_9	72– 94
29[b]	C_5H_{11}	C_5H_{11}	62– 90
30[b]	C_5H_{11}	C_6H_{13}	67– 93
31[b]	C_5H_{11}	C_7H_{15}	55– 89
32[b]	C_5H_{11}	C_8H_{17}	64– 89
33[b]	C_6H_{13}	CH_3	62S68N107
34[b]	C_6H_{13}	C_2H_5	66S70N108
35	C_8H_{17}	CH_3	86S92N 98
36[b]	C_8H_{17}	C_8H_{17}	73S82N 93

[a] Unlabelled transitions are nematic temperature ranges. All others are suitably denoted.

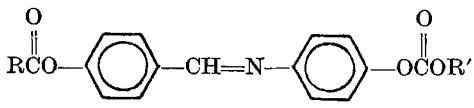
[b] A satisfactory elemental analysis was obtained for this compound.

TABLE 2 

No.	*n*–R	*n*–R′	Range (°C)[a]
37	CH_3	CH_3	101–113
38	CH_3	C_2H_5	118–135
39	CH_3	C_3H_7	92–113
40	CH_3	C_4H_9	101–120
41	CH_3	C_5H_{11}	91–110
42	CH_3	C_6H_{13}	86–112
43	CH_3	C_7H_{15}	96–106
44	CH_3	C_8H_{17}	90–107
45	CH_3	C_9H_{19}	94–105
46	C_2H_5	CH_3	105–121
47	C_2H_5	C_2H_5	106–142
48	C_2H_5	C_3H_7	86–111
49	C_2H_5	C_4H_9	98–118
50	C_2H_5	C_5H_{11}	97–108
51	C_2H_5	C_6H_{13}	81–111
52	C_2H_5	C_7H_{15}	87–101
53	C_2H_5	C_8H_{17}	92–104
54	C_2H_5	C_9H_{19}	84–106
55	C_3H_7	CH_3	104 (91)
56	C_3H_7	C_2H_5	114–117
57	C_3H_7	C_3H_7	101 (97)
58	C_3H_7	C_4H_9	102–110
59	C_3H_7	C_5H_{11}	75–101
60	C_3H_7	C_6H_{13}	86–103
61	C_3H_7	C_7H_{15}	91–100
62	C_3H_7	C_8H_{17}	86–101
63	C_3H_7	C_9H_{19}	90– 99
64	C_4H_9	CH_3	79– 89
65	C_4H_9	C_2H_5	88–109
66	C_4H_9	C_3H_7	91– 95
67	C_4H_9	C_4H_9	93–108
68	C_4H_9	C_5H_{11}	84–100
69	C_4H_9	C_6H_{13}	92–102
70	C_4H_9	C_7H_{15}	81– 98
71	C_4H_9	C_8H_{17}	88–100

No.	*n*-R	*n*-R′	Range (°C)[a]
72	C_4H_9	C_9H_{19}	83– 94
73	C_5H_{11}	CH_3	64– 83
74	C_5H_{11}	C_2H_5	96–107
75	C_5H_{11}	C_3H_7	84–109
76	C_5H_{11}	C_4H_9	70–102
77	C_5H_{11}	C_5H_{11}	69– 96
78	C_5H_{11}	C_6H_{13}	77– 99
79	C_5H_{11}	C_7H_{15}	71– 97
80	C_5H_{11}	C_8H_{17}	69– 97
81	C_5H_{11}	C_9H_{19}	74– 96
82	C_6H_{13}	CH_3	71– 83
83	C_6H_{13}	C_2H_5	80–104
84	C_6H_{13}	C_3H_7	74– 90
85	C_6H_{13}	C_4H_9	73–100
86	C_6H_{13}	C_5H_{11}	63– 96
87	C_6H_{13}	C_6H_{13}	73– 99
88	C_6H_{13}	C_7H_{15}	77– 95
89	C_6H_{13}	C_8H_{17}	69S77N98
90	C_6H_{13}	C_9H_{19}	66S78N94
91	C_7H_{15}	CH_3	78– 84
92	C_7H_{15}	C_2H_5	89–101
93	C_8H_{17}	CH_3	68– 82
94	C_8H_{17}	C_2H_5	84–103
95	C_8H_{17}	C_3H_7	74– 90
96	C_8H_{17}	C_4H_9	68– 98
97	C_8H_{17}	C_5H_{11}	63S65N94
98	C_8H_{17}	C_6H_{13}	66S76N98
99	C_8H_{17}	C_7H_{15}	63S78N94
100	C_8H_{17}	C_8H_{17}	69S87N99
101	C_8H_{17}	C_9H_{19}	71S89N93

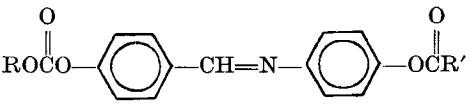
[a] Unlabelled transitions are nematic temperature ranges. All others are suitably denoted.

TABLE 3 

No.	*n*–R	*n*–R′	Range (°C)[a]
102[b]	CH_3	CH_3	116–137
103[b]	CH_3	C_4H_9	63– 81
104[b]	CH_3	C_5H_{11}	92 (92)
105[b]	C_2H_5	CH_3	128–138
106[b]	C_2H_5	C_2H_5	110–131
107[b]	C_2H_5	C_3H_7	95–112
108[b]	C_2H_5	C_4H_9	94–105
109[b]	C_2H_5	C_5H_{11}	86–102
110[b]	C_3H_7	CH_3	73–133
111[b]	C_3H_7	C_2H_5	65–127
112[b]	C_3H_7	C_3H_7	91–110
113[b]	C_3H_7	C_4H_9	88–106
114[b]	C_3H_7	C_5H_{11}	76–103
115[b]	C_4H_9	CH_3	52–115
116[b]	C_4H_9	C_2H_5	69–107
117	C_4H_9	C_3H_7	64– 98
118[b]	C_4H_9	C_4H_9	47– 97
119[b]	C_4H_9	C_5H_{11}	49– 94
120	C_4H_9	C_6H_{13}	64– 96
121[b]	C_4H_9	C_7H_{15}	59– 92
122[b]	C_4H_9	C_8H_{17}	61– 92
123[b]	C_5H_{11}	CH_3	65–118
124	C_5H_{11}	C_2H_5	67–120
125[b]	C_5H_{11}	C_3H_7	66–102
126[b]	C_5H_{11}	C_4H_9	66–102
127[b]	C_5H_{11}	C_5H_{11}	58– 99
128[b]	C_6H_{13}	CH_3	79–112

[a] Unlabelled transitions are nematic temperature ranges. All others are suitably denoted.

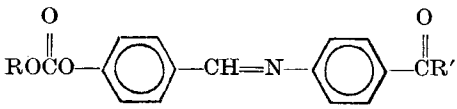
[b] A satisfactory elemental analysis was obtained for this compound.

TABLE 4 

No.	*n*–R	*n*–R′	Range (°C)[a]
129	CH_3	CH_3	119–128
130	C_2H_5	CH_3	113–143
131	C_3H_7	CH_3	93–104
132	C_4H_9	CH_3	84– 94
133[b]	C_4H_9	C_2H_5	116S123N134
134	C_4H_9	C_3H_7	65S76N118
135	C_4H_9	C_4H_9	74S79N103
136	C_5H_{11}	CH_3	96 (89)
137	C_5H_{11}	C_4H_9	72S76N98
138	C_6H_{13}	CH_3	90 (88)
139	C_7H_{15}	CH_3	88 (86)
140	C_8H_{17}	CH_3	90 (87)

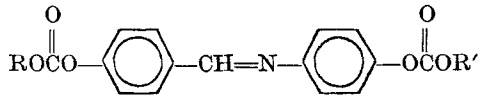
[a] Unlabelled transitions are nematic temperature ranges. All others are suitably denoted.

[b] A satisfactory elemental analysis was obtained for this compound.

TABLE 5 

No.	*n*–R	*n*–R′	Range (°C)[a]
141	CH_3	CH_3	110 (110)
142	CH_3	C_2H_5	130–142
143	CH_3	C_3H_7	100–116
144	CH_3	C_4H_9	121–122
145	C_2H_5	CH_3	119 (111)
146	C_2H_5	C_2H_5	131–145
147	C_2H_5	C_3H_7	105–118
148	C_2H_5	C_4H_9	113–131
149	C_3H_7	CH_3	114 (94)
150	C_3H_7	C_2H_5	117–134
151	C_3H_7	C_3H_7	101–104
152	C_3H_7	C_4H_9	109–115
153	C_4H_9	CH_3	85– 90
154	C_4H_9	C_2H_5	105S106N130
155	C_4H_9	C_3H_7	85S102N104
156	C_4H_9	C_4H_9	83S115N116
157	C_5H_{11}	CH_3	96 (93)
158	C_5H_{11}	C_2H_5	107S110N123
159	C_5H_{11}	C_3H_7	80S90N102
160	C_5H_{11}	C_4H_9	80S115
161	C_6H_{13}	CH_3	84S87
162	C_6H_{13}	C_2H_5	92S118N123
163	C_6H_{13}	C_3H_7	76S106
164	C_6H_{13}	C_4H_9	66S117
165	C_7H_{15}	CH_3	74– 83
166	C_7H_{15}	C_2H_5	91S94N126
167	C_7H_{15}	C_3H_7	77S107
168	C_7H_{15}	C_4H_9	76S116
169	C_8H_{17}	CH_3	80S91N96
170	C_8H_{17}	C_2H_5	97S128
171	C_8H_{17}	C_3H_7	73S111
172	C_8H_{17}	C_4H_9	81S121

[a] Unlabelled transitions are nematic temperature ranges. All others are suitably denoted.

TABLE 6 

No.	*n*–R	*n*–R′	Range (°C)[a]
173[b]	CH_3	CH_3	116–143
174[b]	CH_3	C_3H_7	106–111
175[b]	CH_3	C_5H_{11}	98–100
176[b]	C_2H_5	CH_3	86–131
177[b]	C_2H_5	C_2H_5	91–127
178[b]	C_2H_5	C_6H_{13}	46– 81
179[b]	C_2H_5	C_7H_{15}	73– 79
180[b]	C_2H_5	C_8H_{17}	68– 73
181[b]	C_3H_7	CH_3	71–110
182[b]	C_3H_7	C_2H_5	59–108
183	C_3H_7	C_3H_7	68– 94
184[b]	C_3H_7	C_4H_9	60– 86
185[b]	C_3H_7	C_5H_{11}	58– 84
186[b]	C_3H_7	C_6H_{13}	45– 83
187[b]	C_4H_9	CH_3	77–104
188[b]	C_4H_9	C_3H_7	68– 89
189[b]	C_4H_9	C_4H_9	71– 82
190[b]	C_4N_9	C_5H_{11}	45– 84
191[b]	C_4H_9	C_6H_{13}	42– 85
192	C_4H_9	C_7H_{15}	42– 81
193	C_4H_9	C_8H_{17}	59– 80
194[b]	C_5H_{11}	CH_3	78– 98
195	C_5H_{11}	C_2H_5	78– 87
196[b]	C_5H_{11}	C_4H_9	60– 87
197[b]	C_5H_{11}	C_5H_{11}	55– 86
198[b]	C_6H_{13}	CH_3	75– 96
199	C_6H_{13}	C_4H_9	65– 84

[a] Unlabelled transitions are nematic temperature ranges. All others are suitably denoted.

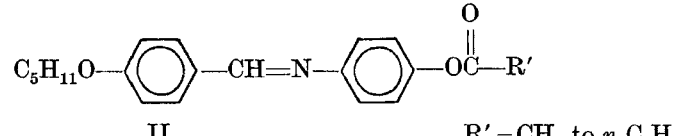
[b] A satisfactory elemental analysis was obtained for this compound.

above a similar plot of transition temperatures for members with odd-numbered carbon chains. Such a pattern is well documented[5] for many homologous series. Also, the N → I transition temperatures gradually decrease with increasing carbon chain length. This pattern is often typical but exceptions are known: N → I transition temperatures increase with increasing carbon chain length for N-(*p*-*n*-alkoxybenzylidene)-*p*′-aminobiphenyls,[5] N-(*p*-*n*-alkoxybenzylidene)-*p*′-aminoacetophenones,[15] and N-(*p*-*n*-alkoxybenzylidene)-*p*′-butylanilines.[16]

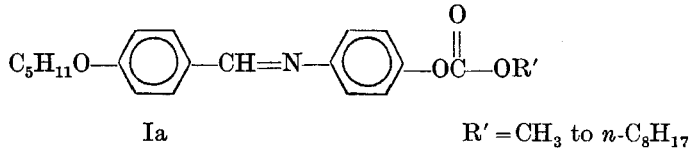
Secondly, the pattern of C → N transition temperatures is typically more random in nature than the N → I transitions, but the fit of the plots of even–odd transition temperatures obtained from a treatment similar to that discussed for the N → I transitions is quite good, particularly for Series Ia. This would substantiate the contention[18] that the controlling factor for the course of C → N transitions into and from the nematic phase is the same, viz., the packing density as controlled by the configurational pattern of the alkyl chains, but that in *most* series the effect of the packing pattern of the alkyl chains becomes evident near the mesomorphic-to-isotropic transition only.

Thirdly, the N → I temperature ranges for Series Ia are lower than Series Ib.

Figure 2 shows a plot of the C → N and N → I transition temperatures for N-(*p*-pentyloxybenzylidene)-*p*′-acyloxyanilines[17] (II) along with the corresponding data for compounds of Series Ia.



II $R' = CH_3$ to n-C_8H_{17}



Ia $R' = CH_3$ to n-C_8H_{17}

It is apparent that C → N and N → I transition temperatures are lower for compounds of Series Ia than compounds II, with the exception of the C → N transitions of the compounds wherein $R' = CH_3$ and C_2H_5. It can be seen that a plot of transition tempera-

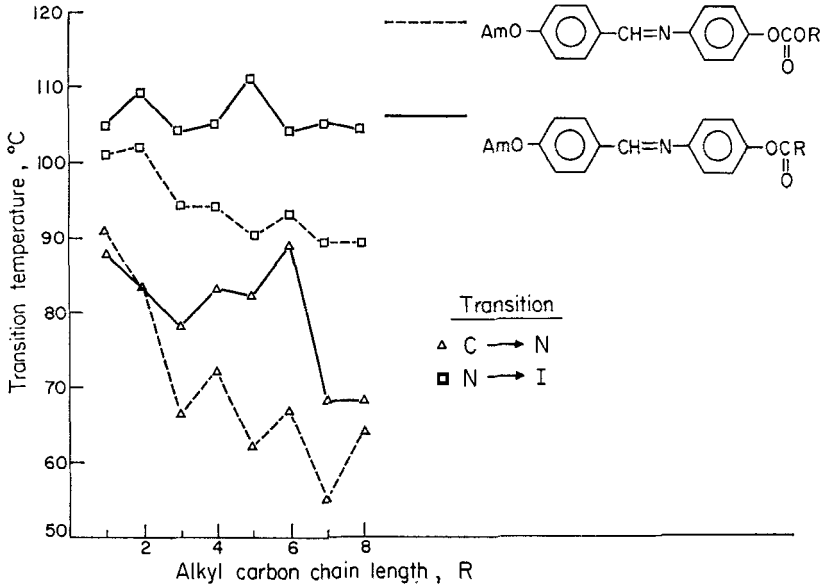
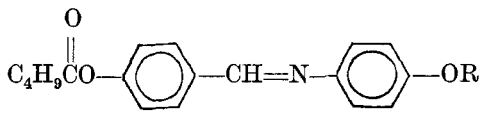


Figure 2. Transition temperatures for *p*-pentyloxy-*p'*-alkoxycarbonyloxy anils vs. *p*-pentyloxy-*p'*-acyloxy anils.

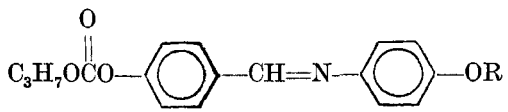
tures *vs.* total number of atoms in the substituent chain will give the same result.

Figure 3 shows a comparison of transition temperatures for N-(*p*-valeryloxybenzylidene)-*p'*-alkoxyanilines (III)[18] and N-(*p*-



III

propoxycarbonyloxybenzylidene)-*p'*alkoxy anilines (Ib). The *p*-substituent of the benzylidene part of the molecule in each case has



Ib R = CH_3 to *n*-C_9H_{19}

the same number of atoms in the " backbone " of the substituent. Both series exhibit a typical alternating trend for the N → I transitions and, as in examples discussed above, the carbonato series has

overall lower N → I transitions. The higher members of the carbonato series also show the lower crystal-to-mesomorphic transitions. The thermal destabilization of the mesophase of anils containing an alkyl carbonato group relative to anils containing an acyloxy group was recently noted[17] for one pair of anils in which the acyloxy and alkyl carbonato substituents were located on the benzylidene ring.

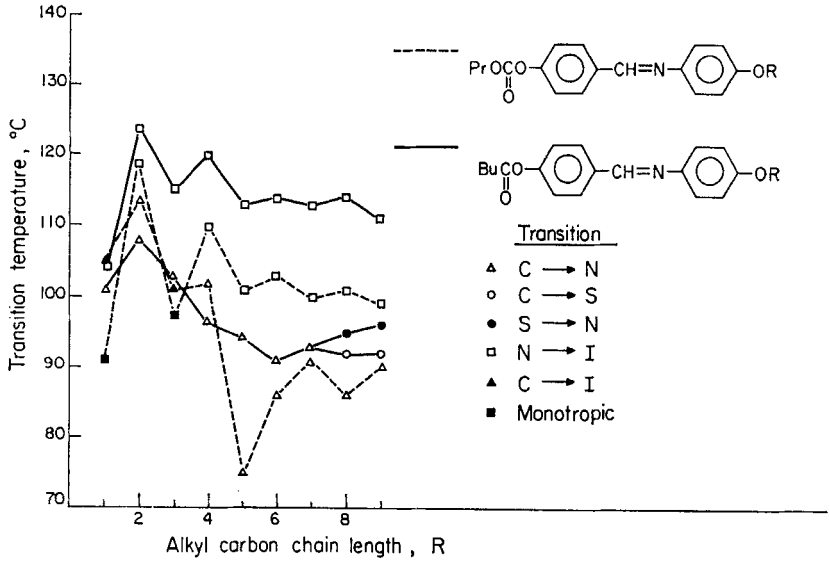


Figure 3. Transition temperatures for *p*-propoxycarbonyloxy-*p'*-alkoxy anils vs. *p*-valeryloxy-*p'*-alkoxy anils.

The transition temperatures and mesomorphic ranges of pairs of anils with functionally equivalent substituents with nonidentical chain length reveal interesting trends when the positions of entire substituents or their alkyl chain portions are interchanged. The pairs of compounds which will be discussed are represented by Formula I and the specific data given for each compound will be the compound number as listed in Tables 1 to 6, the *X*- and *Y*-substituents, the nematic mesomorphic range, and the breadth or extent of the mesomorphic range (ΔT_M).

Compounds 184 and 191 (Series If) have broader mesomorphic ranges than their respective counterparts (188 and 199), which have

the same functionality but with interchanged alkyl groups. Within each pair of di-carbonato-substituted anils (184 and 188, 191 and 199), the total number of substituent chain atoms is the same. The

No.	X	Y	Range (°C)	ΔT_M (°C)
184	C_3H_7OCOO	C_4H_9OCOO	60–86	26
188	C_4H_9OCOO	C_3H_7OCOO	68–89	21
191	C_4H_9OCOO	$C_6H_{13}OCOO$	42–85	43
199	$C_6H_{13}OCOO$	C_4H_9OCOO	65–84	19

compounds with the longer chain length in the Y-substituent (184 and 191) have the lower C → N transition temperature, but the N → I transition temperatures within each pair of anils are similar. In contrast to pairs of di-carbonato-substituted anils in which both members have similar N → I transition temperatures, for pairs of anils compared below in which each member contains one carbonato substituent, the member with the Y-carbonato-substituent without exception has the lower N → I transition temperature.

Trends in breadth of range hold for anils with nonidentical functional group substituents of differing total chain length. Compound 16 (Series Ia), with a Y-substituent chain length of 8, has lower transition temperatures and a broader mesomorphic range than does Compound 75 (Series Ib) with a Y-substituent chain length of 4. Compounds 22 (Series Ia) and 85 (Series Ib) exhibit this same interrelationship. Exchanging an ester group for the alkoxy group produced the same result. Compounds 119 and 102 (Series Ic) have lower transition temperatures and broader mesomorphic ranges

No.	X	Y	Range (°C)	ΔT_M (°C)
16	C_3H_7O	$C_5H_{11}OCOO$	59–90	31
75	$C_5H_{11}OCOO$	C_3H_7O	84–109	25
22	C_4H_9O	$C_6H_{13}OCOO$	56–91	35
85	$C_6H_{13}OCOO$	C_4H_9O	73–100	27
119	C_4H_9COO	$C_5H_{11}OCOO$	49–94	45
137	$C_5H_{11}OCOO$	C_4H_9COO	72S76N98	26
102	CH_3COO	C_4H_9OCOO	63–81	18
132	C_4H_9OCOO	CH_3COO	86–93	7

than their functionally interchanged counterparts, 137 and 132 (Series Id), respectively, which have shorter chain lengths in the Y-substituent.

If the number of atoms in the " backbone " of the substituents is the same but the p-substituent functionality is different, a comparison of Compounds 27 and 59 shows that, for alkoxy vs. carbonato, the carbonato group at the Y-position (27, Series Ia) leads to a broader mesomorphic range with lower transition temperatures. However, the differences in this comparison are not as large as with the previous examples, as might be expected. If the corresponding di-carbonato (183, Series If), di-acyloxy (200), and di-alkoxy (201) compounds are compared, the di-carbonato compound has a comparable mesomorphic range with Compounds 27 and 59; in contrast,

No.	X	Y	Range (°C)	ΔT_M (°C)
27	$C_5H_{11}O$	C_3H_7OCOO	66–94	28
59	C_3H_7OCOO	$C_5H_{11}O$	75–101	26
183	C_3H_7OCOO	C_3H_7OCOO	68–94	26
200	C_4H_9COO	C_4H_9COO	112–115	3
201	$C_5H_{11}O$	$C_5H_{11}O$	113	0

the di-acyloxy compound[19] has only a short nematic range from 112–115 °C and the di-alkoxy compound[19] is not mesomorphic in our hands and melts at 113 °C. Kast[4] reports 201 to be monotropic at 103 °C. These examples testify to the desirable characteristics of the carbonato group with respect to liquid-crystalline properties.

A further extension of this comparison can be made between compounds of nonidentical substituent functionality in which the substituent of the shorter " backbone " chain length is the carbonato substituent. In such comparisons, the position of the carbonato substituent again seems important. Compounds 26 and 17 (Series Ia), with carbonato substituents in the Y-position that have " backbone " chain lengths one atom shorter than the alkoxy X-substituents, have lower and broader mesomorphic ranges than their reverse counterparts 50 and 40 (Series Ib), respectively. The same trend may hold true for compounds with carbonato Y-substituents that have a " backbone " chain length two atoms shorter than the alkoxy X-substituents. Thus Compound 34 (Series Ia) has a lower

and broader mesomorphic range than does its reverse counterpart 51 (Series Ib); but Compounds 25 vs. 41 show similar ranges. When the *Y*-carbonato substituent is three atoms shorter than the alkoxy *X*-substituent, the trend still holds (33 vs. 42), but when the chain-length difference is increased to five atoms, the mesomorphic range is lower when the carbonato substituent is in the *Y*-position (Compound 35, Series Ia) while the range is broader with the *X*-substituent being carbonato (Compound 44, Series Ib). Thus the range-

No.	*X*	*Y*	Range (°C)	ΔT_M (°C)
26	$C_5H_{11}O$	C_2H_5OCOO	83–102	19
50	C_2H_5OCOO	$C_5H_{11}O$	97–108	11
17	C_4H_9O	CH_3OCOO	69–115	46
40	CH_3OCOO	C_4H_9O	102–120	18
34	$C_6H_{13}O$	C_2H_5OCOO	66–108	42
51	C_2H_5OCOO	$C_6H_{13}O$	81–111	30
25	$C_5H_{11}O$	CH_3OCOO	91–105	14
41	CH_3OCOO	$C_5H_{11}O$	91–110	19
33	$C_6H_{13}O$	CH_3OCOO	62–102	45
42	CH_3OCOO	$C_6H_{13}O$	86–112	26
35	$C_8H_{17}O$	CH_3OCOO	86–98	12
44	CH_3OCOO	$C_8H_{17}O$	90–107	17

broadening effect of a carbonato group in the *Y*-position depends on the relative chain lengths of the *X*- and *Y*-substituents.

These structure–mesomorphic range relationships for appropriately related pairs of anils, are summarized below.

1) In dicarbonato-substituted anils, the compound with the longer chain length in the *Y*-position has the broader mesomorphic range with a lower C → N and a similar N → I transition temperature.

2) For anils with one carbonato substituent, the C → N and N → I transition temperatures are lower for the compound in which the carbonato substituent is in the *Y*-position.

3) For anils with one carbonato and one alkoxy or acyloxy substituent in which the carbonato-substituent chain length is the longer, a lower and broader mesomorphic range exists for the compound in which the carbonato substituent is in the *Y*-position (Formula I).

4) For anils with one carbonato and one alkoxy substituent of

identical chain length, the compound with the *Y*-carbonato-substituent exhibits the lower and broader mesomorphic range.

5) For anils with one carbonato and one alkoxy substituent in which the carbonato chain length is the shorter, the *Y*-carbonato-substituted anil usually has the lower and broader mesomorphic range in the cases studied, when the difference in substituent chain length is not large; however, when the total atom difference in the substituent chain length is five, the *Y*-carbonato-substituted anil has the lower but narrower mesomorphic range.

6) The mesomorphic range of a carbonato-substituted anil is generally lower and broader, relative to an anil with substituents of the same length other than carbonato. Carbonato substituents promote mesomorphic properties better than acyloxy substituents which in turn are better than alkoxy substituents.

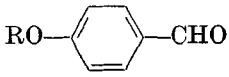
3. Experimental Section

Quantitative elemental analysis, coupled with mass spectrometry in some cases, was employed as an indication of compound purity for a large number of compounds. Our intention in this study was to efficiently survey a large number of related anils in search of ambient or near-ambient nematogens while noting intra- and interseries trends in thermal behavior. The rigorous demonstration of the purity of every compound was not our primary concern; however, compound purity was judged to be greater than 99% in most cases. Melting points were determined with a Thomas–Hoover melting point apparatus and are uncorrected.

1. *p*-Alkoxybenzaldehydes

A solution of *p*-hydroxybenzaldehyde (2.46 mol) and potassium hydroxide (2.5 mol) in 1.2 liters of ethanol (anhydrous) was stirred and heated at 30–40 °C while a 1-iodoalkane (2.5 mol) was added slowly (1–2 h), after which the mixture was refluxed for 3 h. The mixture was cooled to 40 °C and poured into 3–3.5 liters of water. The oily product was extracted with ethyl ether and the combined

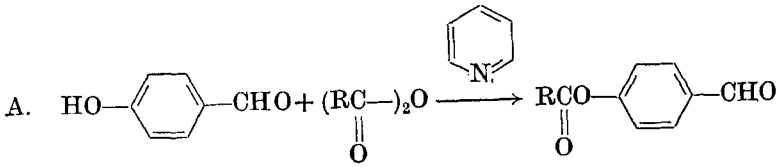
extracts were dried (sodium sulfate) and concentrated at reduced pressure to give an oil. This material was distilled to give a red product which was decolorized with zinc dust (1 h) and redistilled.



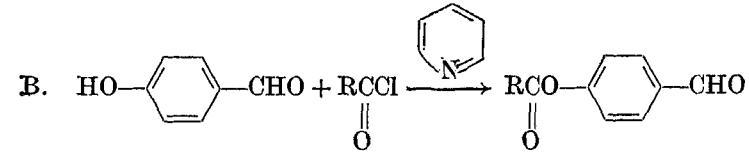
R	bp (°C)	Yield (%)[a]
C_2H_5	134–6°/17 mm	67
C_3H_7	141–3°/20 mm	48
C_4H_9	155–7°/20 mm	64
C_5H_{11}	163–6°/10 mm	54
C_6H_{13}	177–80°/10 mm	71
C_7H_{15}	143–6°/5 mm	58
C_8H_{17}	141–4°/0.1 mm	40
C_9H_{19}	163–6°/0.5 mm	42

[a] All ethers were 98% min. purity by titration with hydroxylamine.

2. *p*-ACYLOXYBENZALDEHYDES

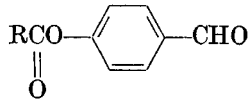
A. 

To a cooled (20–25 °C) solution of *p*-hydroxybenzaldehyde (2.46 mol) in 1.2 kg of pyridine an acid anhydride (2.46 mol) was added dropwise (1.5 h). The mixture was stirred for an additional 0.5 h before it was poured into 3 liters of cold water. The oily product was extracted with benzene and the combined extracts were washed twice with 50 °C water, dried, and concentrated at reduced pressure to give an orange oil which was distilled to give purified product.

B. 

To a cooled (20–25 °C) solution of *p*-hydroxybenzaldehyde (1.81 mol) and pyridine (2.0 mol) in 1 liter of benzene an acid chloride

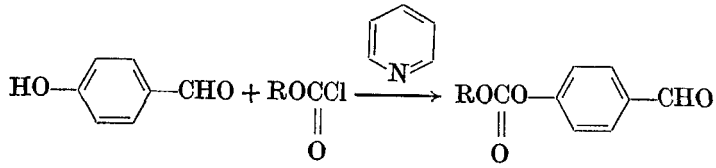
(1.98 mol) was added dropwise (1.5 h). The mixture was stirred for an additional 0.5 h before it was poured into 3 liters of cold water. The product was extracted with benzene and the combined extracts were washed twice with 50 °C water, dried, and concentrated at reduced pressure to give an orange oil which was distilled to give a purified product. The colorless product was stored under nitrogen.



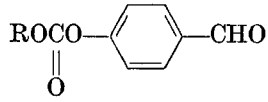
R	bp (°C)	n_D^{20}	Yield (%)[a]	Method
CH_3	142–4°/13 mm	1.5401	69	A
C_2H_5	152.5–4.5°/8 mm	1.5303	78	B
C_3H_7	154–5°/8 mm	1.5215	76	B
C_4H_9	166–9°/9 mm	1.5170	76	B
C_5H_{11}	115–6°/0.5 mm	1.5130	67	B
C_6H_{13}	—	—	92	B

[a] All esters were 98% min. purity by titration with hydroxylamine.

3. *p*-Alkoxycarbonyloxybenzaldehydes



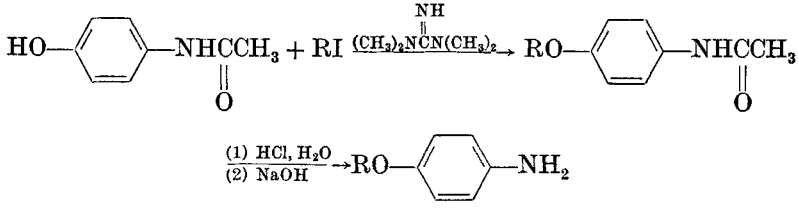
To a cooled (15–25 °C) solution of *p*-hydroxybenzaldehyde (1.5 mol) in 1.4 liters of benzene was added pyridine (1.75 mol) followed by the dropwise addition (3 h) of an alkyl chloroformate (1.58 mol). The mixture was stirred with cooling for an additional 0.5 h and then at room temperature for 2 h. The solid pyridine hydrochloride which formed was removed by filtration and washed with benzene. The combined benzene solution of the product and washings were combined, decolorized with carbon, and concentrated at low heat and reduced pressure to give and oily product. This material was purified by distillation if possible or recrystallized from hexane.



R	bp (mp) (°C)	n_D^{20}	Yield (%)[a]
CH_3	mp 34–6°	—	62
C_2H_5	bp 110°/0.8 mm mp 20–2°	1.5240	62
C_3H_7	bp 121–3°/0.5 mm mp 5–7°	1.5165	88
C_4H_9	bp 128–30°/0.5 mm mp 3–6°	1.5130	85
C_5H_{11}	bp 1–3°	1.5105	82
C_6H_{13}	mp 0–2°	1.5090	84
C_7H_{15}	—	—	91
C_8H_{17}	mp 9–11°	—	92

[a] All carbonates were 98% min. purity by titration with hydroxylamine.

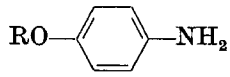
4. *p*-ALKOXYANILINES



To a suspension of 4′-hydroxyacetanilide (1.51 mol) in 1.2 liters of ethanol (anhydrous) was added (5 min) tetramethylguanidine (1.52 mol). The resulting solution was heated at 50 °C for 0.5 h before an iodoalkane (1.52 mol) was added slowly (0.5 h) as the temperature was maintained at 50–60 °C. The mixture was then stirred overnight at 70 °C, cooled to room temperature, and poured into 7 liters of cold water. The intermediate 4′-alkoxyacetanilide which formed was removed by filtration, washed with water, and air dried at 40–50 °C.

A mixture of the 4-alkoxyacetanilide (1.46 mol), 700 ml of water, and 420 ml of concentrated hydrochloric acid was stirred overnight at 90–95 °C and cooled to room temperature. The mixture was made basic with 50% sodium hydroxide solution as the temperature was

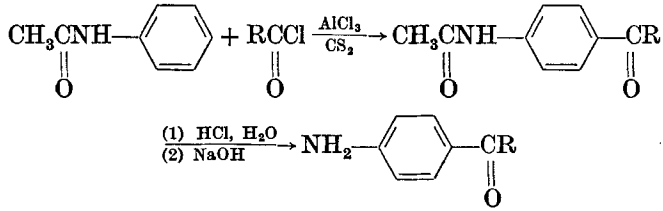
kept below 20 °C with external cooling. The oily product was extracted with ethyl ether and the combined extracts were dried (magnesium sulfate) and concentrated at reduced pressure to give an oil which was purified by distillation. The colorless product was stored under nitrogen.



R	bp (°C)	n_D^{20}	Yield (%)[a]	mp of acetanilide
C_3H_7	120–2°/4 mm	1.5490	58	108–110°
C_4H_9	130–2°/4 mm	1.5385	71	96–100°
C_5H_{11}	142–4°/5 mm	1.5315	69	85–86°
C_6H_{13}	167–9/5 mm; mp 44–6°	—	61	105–106°
C_7H_{15}	181–2°/10 mm	—	48	87–88°
C_8H_{17}	151–2°/1 mm	—	47	92–93°
C_9H_{19}	158–9°/1 mm	—	50	68–70°

[a] All ethers were 98% min. purity by nonaqueous titration.

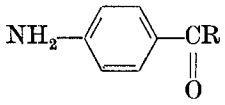
5. *p*-AMINOPHENONES



To a vigorously stirred, cooled (20 °C) mixture of aluminum chloride (5.3 mol) and 1.3 liters of carbon disulfide was added slowly (30–50 min) an acid chloride (1.5 mol). Then acetanilide (1.48 mol) was added in small portions as the temperature was kept at 25–30 °C. The mixture was stirred for an additional hour, refluxed for 96 h, and cooled.

The carbon disulfide layer was separated and evaporated to yield some intermediate which was combined with that obtained as a precipitate from pouring the remainder of the reaction mixture on a mixture of 4 kg of ice and 1 liter of concentrated hydrochloric acid.

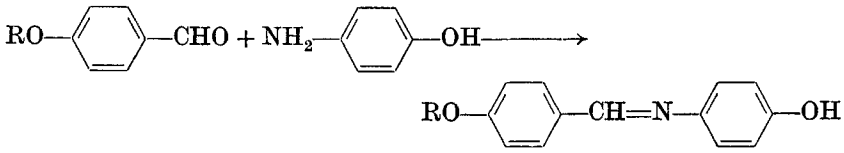
A suspension of the solid intermediate 4′-acetamidophenone in 1 liter of concentrated hydrochloric acid was warmed slowly to 50 °C, the entrapped carbon disulfide was distilled from the mixture as the temperature was allowed to reach 75–80 °C, and the mixture was refluxed overnight before it was cooled and poured into a 10% sodium hydroxide solution. The product which precipitated was dissolved in ethyl ether, dried (magnesium sulfate), and concentrated at reduced pressure until the product crystallized.



R	mp (°C)	Yield (%)[a]
CH_3	106–8°	68
C_2H_5	141–3°	41
C_3H_7	92–4°	53
C_4H_9	71–3°	22

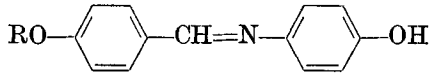
[a] All phenones were 98% min. purity by nonaqueous titration.

6. *p*-ALKOXY, *p*-ACYLOXY, AND *p*-ALKOXYCARBONYLOXYBENZYLIDENEAMINOPHENOLS

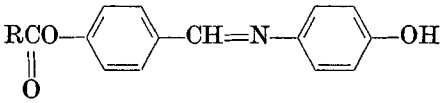


R = alkyl, acyl or alkoxycarbonyl

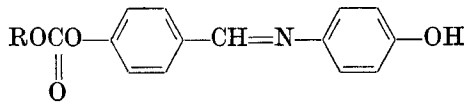
To a hot solution of *p*-aminophenol (0.88 mol) in 2 liters of ethanol (anhydrous) was added a *p*-alkoxy, *p*-acyloxy, or *p*-alkoxycarbonyloxybenzaldehyde (0.88 mol). The mixture was refluxed for 0.5 h, filtered hot to remove a small amount of dark insoluble material, and cooled to 10 °C to precipitate the product which was recrystallized from 2-butanone.



R	mp (°C)	Yield (%)
CH_3	192–4°	82
C_2H_5	189–91°	91
C_3H_7	184–6°	82
C_4H_9	154–6°	89
C_5H_{11}	146–8°	75
C_6H_{13}	152–4°	94
C_7H_{15}	136–8°	91
C_8H_{17}	129–31°	85
C_9H_{19}	131–3°	94



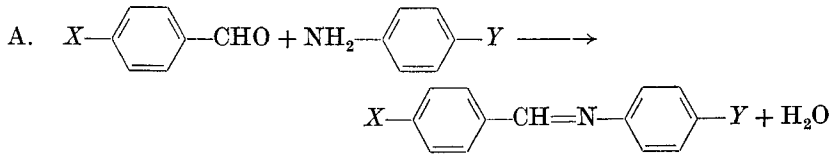
R	mp (°C)	Yield (%)
CH_3	185–7°	72
C_2H_5	183–5°	66
C_3H_7	174–6°	64
C_4H_9	137–8°	60
C_5H_{11}	126–7°	83
C_6H_{13}	120–1°	63
C_7H_{15}	126–8°	71
C_8H_{17}	128–30°	68



R	mp (°C)	Yield (%)
CH_3	171–2°	78
C_2H_5	168–70°	81
C_3H_7	161–3°	84
C_4H_9	110–112°	59
C_5H_{11}	102–4°	40
C_6H_{13}	99–101°	40
C_7H_{15}	105–7°	63
C_8H_{17}	109–111°	74

7. Liquid Crystalline Schiff Bases

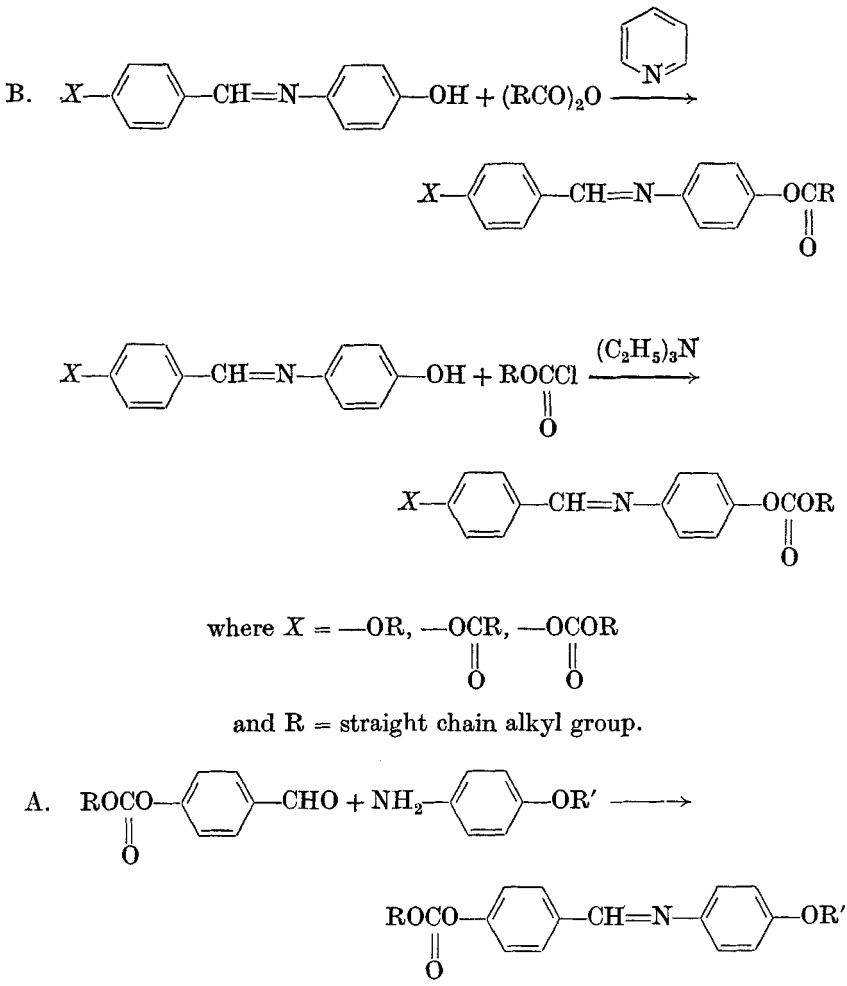
The liquid-crystalline Schiff bases included in this study were prepared by either the condensation of the appropriately *p*-substituted benzaldehyde with a *p*-substituted aniline or by treatment of a *p*-substituted benzylideneaminophenol with an acid anhydride or a chloroformate in the presence of an acid acceptor, as shown in the following general reactions:

A. 

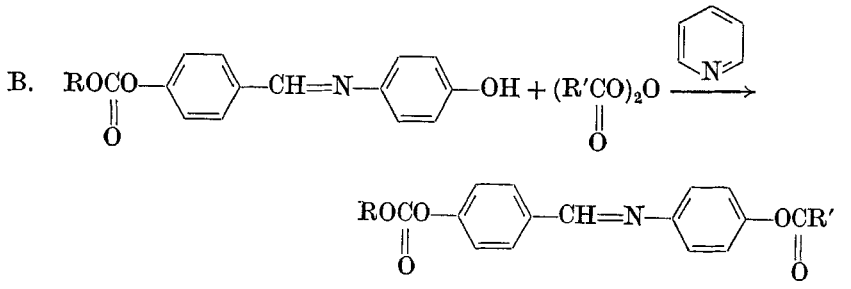
where X = —OR, —OCR, —OCOR

and Y = —OR, —CR

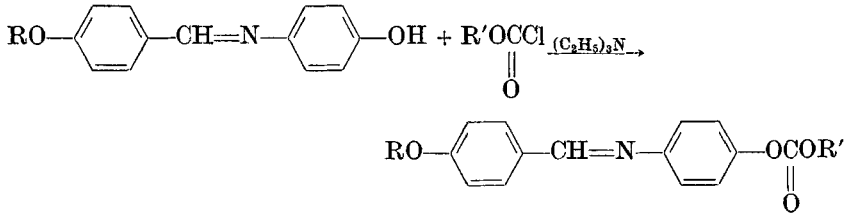
(R = straight chain alkyl group)



To a solution of a *p*-alkoxycarbonyloxybenzaldehyde (0.1 mol) in 50 ml of ethanol (anhydrous) was added a *p*-alkoxyaniline (0.1 mol.) The mixture was heated on a steam bath to 70 °C for 3–4 min and allowed to cool. The product which precipitated was removed by filtration, rinsed with cold ethanol, washed thoroughly with petroleum ether, and recrystallized twice from ethanol (decolorizing carbon). A summary of the Schiff bases prepared by this method is given in Tables 2 and 5.



To a suspension of a *p*-[N-(*p*-alkoxycarbonyloxybenzylidene)-amino]phenol (0.2 mol) and 400 ml of benzene was added pyridine (0.2 mol) followed by an acid anhydride (0.2 mol) before the mixture was heated at reflux for 12–18 h. The cooled mixture was washed thoroughly twice with 40 °C water, dried (magnesium sulfate), and concentrated at reduced pressure to give a crystalline mass which was recrystallized twice from 2-propanol. The Schiff bases prepared in this manner are summarized in Table 4.



To a mixture of a *p*[N-(*p*-alkoxybenzylidene)amino]phenol (0.1 mol) and 300 ml of ethyl ether was added triethylamine (0.5 mol). This mixture was refluxed for 0.5 h and cooled before a solution of an alkyl chloroformate (0.1 mol) in 50 ml of ethyl ether was added dropwise (5 min) and the mixture was refluxed for 16–18 h. The precipitated triethylamine hydrochloride was removed by filtration and washed with ethyl ether. The combined filtrates and washings were combined and evaporated to dryness at reduced pressure to yield the product which was recrystallized twice from ethanol (anhydrous). The Schiff bases prepared in this manner are summarized in Tables 1, 3 and 6.

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18. Compounds of this class of anils have been prepared in this laboratory. Figure 3 contains the transition temperatures for those compounds discussed.
19. Compounds 200 and 201 were prepared in this laboratory.