Liquid Crystals. IV. Effects of Terminal Substituents on the Nematic Mesomorphism of *p*-Phenylene Dibenzoates[1]

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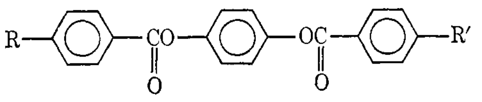
Received January 25, 1973

New *p*-phenylene dibenzoates with various end groups were prepared and their phase transition temperatures determined. The data for these compounds and for other terminally substituted *p*-phenylene dibenzoates described in the literature were then examined for trends in nematic liquid crystalline behavior. Only 7 of the 63 esters do not exhibit a nematic mesophase. The marked tendency of this molecular system to be nematic is further shown by the mesomorphism of three esters having only one terminal substituent. Of the end groups for which data are available, long-chain alkoxy groups are most effective at lowering the melting point; CN, NO_2, COOMe, and Br are most effective at raising it. The highest nematic–isotropic transition temperatures are produced by CN, COOMe, MeO, and COOEt, and the lowest by COO-*n*-Bu, *i*-Pr, cyclohexoxy, and *i*-BuO. Unsymmetrical di-*n*-alkoxy esters are the lowest melting *p*-phenylene dibenzoates and have the broadest nematic temperature ranges. An attempt is made to rationalize the data, and analogies with other nematic molecular systems are discussed. In the course of the investigation, new para-substituted benzoic acids and *p*-hydroxyphenyl benzoates were also synthesized.

Attempts to correlate the properties of compounds with their molecular structures are common in chemical research. A familiar example is the systematic variation of substituent groups on a physiologically active parent compound to determine the effect of these changes on activity. Mesomorphic (liquid crystalline)[2-4] molecular systems have been investigated in a similar manner to ascertain the effects of structural variations on the temperature range over which the mesophase is stable. Sometimes, the objective is to "tailor" the range to fit a particular application. Usually, there is also the broader goal of finding correlations between specific structural modifications and changes in liquid crystallinity that might be applicable in some degree to other mesomorphic systems. Ideally, if the latter goal is considered, the original compound's mesophase should exist over a broad temperature range. Otherwise, even minor alterations in structure may destroy mesomorphism altogether. If most structural changes accomplish this destruction, their deleterious effect is established, but the relative extent to which they are disruptive remains unknown.

p-Phenylene di-*n*-alkoxybenzoates (**1**, R = R′ = *n*-alkoxy) have been shown[5-7] to exhibit nematic mesophases[2-4] with broad ranges terminating at high temperatures. Introduction of a methyl substituent on the central phenylene ring,[7] two very different terminal alkoxy groups (*e.g.*, CH_3O and *n*-$C_8H_{17}O$),[8] or replacement of the alkoxy end groups by Cl, NO_2, or CO_2Et[6a] do not destroy mesomorphism. These results suggested that the nematic mesophase of system **1** might survive still more drastic structural variations and, therefore, that the system would be excellent for an extensive study of the effects of structural changes on nematic behavior. This paper describes an investigation of major variations of R and R′.



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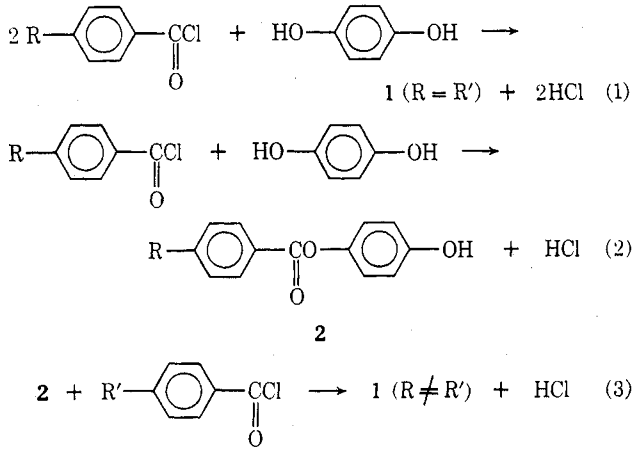
Ten symmetrical and 11 unsymmetrical esters of type **1** were prepared by the processes shown in eq 1–3. During the investigation, three new para-substituted benzoic acids and three new phenols of type **2** were also prepared. The phase transition temperatures of these products were determined using a hot stage polarizing microscope.



Experimental Section

Para-Substituted Benzoic Acids.—The methyl, isopropyl, *tert*-butyl, bromo, chloro, and cyano acids are commercial products. The isobutoxy, cyclohexoxy, and 2-ethoxyethoxy acids were prepared by reaction of ethyl *p*-hydroxybenzoate with the appropriate alkyl bromide and saponification of the resulting ethyl *p*-alkoxybenzoate in ethanolic KOH solution.[5] Recrystallization solvent, yield (based on ethyl *p*-hydroxybenzoate), and melting point data are as follows: *i*-C_4H_9O acid, benzene, 86%, 142°; cyclohexoxy acid, EtOH, 12%, 185°; $EtOCH_2CH_2O$ acid, benzene, 90%, 134°. Apparently, Steinsträsser[9] has prepared the last-named compound, but does not describe its properties.

Benzoyl Chlorides.—Benzoyl and *p*-nitrobenzoyl chloride were purchased. The others were obtained from the corresponding

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[1] (a) This work was supported by a grant from the Research Council of the University of North Carolina at Greensboro and a summer stipend from the university. (b) Previous paper in this series: M. A. Andrews, D. C. Schroeder, and J. P. Schroeder, *J. Chromatogr.*, **71**, 233 (1972).

[2] G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1049 (1957).

[3] G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

[4] A. Saupe, *Angew. Chem., Int. Ed. Engl.*, **7**, 97 (1968).

[5] M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965).

[6] (a) M. J. S. Dewar and R. S. Goldberg, *J. Org. Chem.*, **35**, 2711 (1970); (b) *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

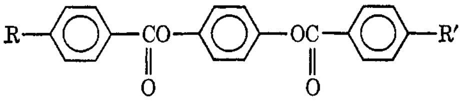
[7] S. L. Arora, J. L. Fergason, and T. R. Taylor, *J. Org. Chem.*, **35**, 4055 (1970).

[8] S. A. Haut, D. C. Schroeder, and J. P. Schroeder, *J. Org. Chem.*, **37**, 1425 (1972).

[9] R. Steinsträsser, *Angew. Chem., Int. Ed. Engl.*, **11**, 633 (1972).

Table I

p-Phenylene Dibenzoates[a]



Registry no.	R	R′	Synthetic method	Recrystn solvent	Yield, %	—Transition temp, °C— Mp	N–I[b]
14210-97-0	H	H	A	EtOH	60	207[c]	*d*
40781-77-9	H	Me	A	EtOH	81	172	*d*
40781-78-0	H	MeO	A	EtOH	76	157	173
40781-79-1	H	*i*-BuO	A	EtOH	90	153.5	*d*
40781-80-4	H	*n*-$C_6H_{13}O$	A	EtOH	89	119	150
40864-79-7	H	$EtOCH_2CH_2O$	A	EtOH	92	134	(117)[e]
40781-81-5	Me	Me	A	Dioxane	63	231.5	236
40781-82-6	*i*-Pr	*i*-Pr	C	EtOH	8	161.5	*d*
40781-83-7	*t*-Bu	*t*-Bu	B	EtOAc	58	204	*d*
40781-84-8	MeO	Me	A	1. EtOH-dioxane 2. EtOH	73	199	265
40781-85-9	MeO	Cl	A	EtOH	93	196	275
40781-86-0	MeO	Br	A	EtOH-dioxane	81	214	277
40781-87-1	MeO	*i*-BuO	A	EtOH	73	155.5	236.5[f]
40781-88-2	MeO	Cyclohexoxy	B	EtOH	89	174	299
40781-89-3	MeO	$EtOCH_2CH_2O$	A	EtOH	60	127[g]	237
40781-90-6	*i*-BuO	*i*-BuO	A	EtOH	75	174	181
40781-91-7	Cyclohexoxy	Cyclohexoxy	B	EtOH	59	203	(163)[e]
40781-92-8	$EtOCH_2CH_2O$	$EtOCH_2CH_2O$	A	EtOH	76	125	188.5
40781-93-9	Br	Br	A	Dioxane	73	255	(252)[e]
40781-94-0	CN	CN	B	Dioxane	74	331.5	353.5
24706-98-7	NO_2	NO_2	B	Dioxane	55	262[h]	281[h]

[a] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table. [b] Nematic–isotropic. [c] Lit. mp 204°: M. T. Bogert and H. P. Howells, *J. Amer. Chem. Soc.*, **52,** 837 (1930). [d] Not liquid crystalline. [e] Monotropic transition observed only on cooling. [f] This compound also exhibited a monotropic transition (see footnote *e*) from nematic to smectic at 125.5°. [g] Another crystalline modification melting at 109.5° to nematic liquid was also observed. [h] Mp 260° and N–I transition temperature 266° have been reported for this compound (ref 6a).

acid by treatment with thionyl chloride at reflux in the presence of pyridine as catalyst. Excess thionyl chloride was distilled to give the acid chloride as a residue product. p-Ethoxyethoxybenzoyl chloride crystallized on cooling as needles, mp 43–45°.

p-Hydroxyphenyl Benzoate (2) Starting Materials.—The p-methoxy- and p-n-hexoxybenzoates had been synthesized earlier by S. A. Haut.[8] p-Hydroxyphenyl benzoate, mp 167° (lit.[10] mp 164°), was prepared from benzoyl chloride and hydroquinone by essentially the same procedure.

p-Phenylene Dibenzoates (1). Method A.—Most of the esters were prepared by the procedure that had proven to be satisfactory earlier.[5,8] Typically, for symmetrical esters, a solution of 0.0060 mol of hydroquinone in 30 ml of dry pyridine was added with swirling to a solution of 0.018 mol of acid chloride in 30 ml of dry pyridine. After standing for 24–48 hr, the mixture was added to 300 ml of 3 N hydrochloric acid. The resulting precipitate was filtered, washed with water, and stirred with 200 ml of 5% aqueous Na_2CO_3 solution for 1 hr. The crude product was recovered by filtration, washed with water and then ethanol, and recrystallized from a suitable solvent. The procedure for unsymmetrical esters was similar except that the reaction was initiated by addition of a solution of the hydroxyphenyl benzoate to a solution of the acid chloride (molar ratio 1:3), both in anhydrous pyridine.

This method was unsuccessful when applied to the preparation of the di-p-isopropyl and di-p-*tert*-butyl benzoates. The only esters isolated were small amounts of p-hydroxyphenyl p-alkyl benzoates (see below). Accordingly, the following procedural modifications were tried.

Method B.—The only change here was to add the reaction mixture to water instead of hydrochloric acid to precipitate the product. The di-*tert*-butyl benzoate was obtained in this manner. The method was subsequently used to prepare several other esters (see Table I). In the synthesis of p-phenylene di-p-cyclohexoxybenzoate, the monoester (see below) was a major by-product.

Method C.—The di-i-propylbenzoate was prepared using classic Schotten–Baumann conditions. p-Isopropylbenzoyl chloride (0.0040 mol) was added with stirring to a solution of 0.0010 mol of hydroquinone and 2.0 g of NaOH in 8 ml of water. After 1.5 hr, the product was recovered by filtration, washed with water, and recrystallized.

In all three methods, excess acyl chloride can be recovered (as the acid) by treatment of the alkaline filtrate and/or wash liquor with excess hydrochloric acid. The results for the dibenzoates are summarized in Table I.

p-Hydroxyphenyl Benzoate (2) Products.—2, R = i-C_3H_7, mp 127°, and 2, R = t-C_4H_9, mp 156°, were the sole products of attempts to prepare the corresponding dibenzoates by method A. The yields were 2 and 4%, respectively. 2, R = cyclohexoxy, mp 133°, was a major by-product (33% yield) in the synthesis of the corresponding dibenzoate by method B. All three compounds were recrystallized from aqueous ethanol.

Transition Temperatures.—These were determined with a Reichert "Thermopan" polarizing microscope equipped with a Kofler micro hot stage. The instrument was calibrated against pure compounds of known melting points.

Analyses.—The elemental microanalyses were performed by Dr. Kurt Eder, Geneva, Switzerland, and by Galbraith Laboratories, Inc., Knoxville, Tenn. Satisfactory analytical data (±0.4% for C and H) were reported for the new p-alkoxybenzoic acids and p-hydroxyphenyl benzoates.

Results and Discussion

The esters in Table I fall into three general categories of end group combinations: R–R, MeO–R, and H–R. In Table II, system **1** esters from this work and from the literature are arranged, within each of the three end-group categories, in order of increasing N–I transition temperature. Of the 42 esters in Table II, representing a wide variation in end groups,

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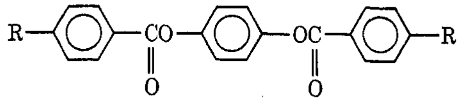
(10) F. Kehrmann, M. Sandoz, and R. Monnier, *Helv. Chim. Acta*, **4,** 941 (1921).

TABLE II

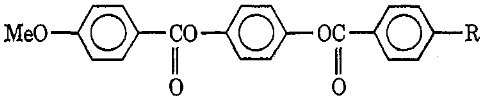
EFFECTS OF TERMINAL SUBSTITUENTS ON NEMATIC-ISOTROPIC TRANSITION TEMPERATURES AND MELTING POINTS OF p-PHENYLENE DIBENZOATES[a]

Symmetrical Esters



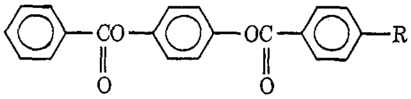
Registry no.	R	N-I temp, °C	Mp, °C
	H		207
	i-Pr		161.5
	t-Bu		204
1819-04-1	COO-*n*-Bu	155[b]	139[b]
	Cyclohexoxy	163	203
	i-BuO	181	174
	$EtOCH_2CH_2O$	188.5	125
24706-96-5	*n*-$C_8H_{17}O$	195[c]	122[c]
1819-00-7	*n*-$C_7H_{15}O$	199[c]	122[c]
24706-99-8	F	199[d]	210[e]
1818-99-1	*n*-$C_6H_{13}O$	213[c]	124[c]
1819-03-0	COO-*n*-Pr	219[b]	193[b]
33903-92-3	*n*-$C_5H_{11}O$	222[f]	145[f]
	Me	236	231.5
1818-98-0	*n*-BuO	241[g]	153[g]
5411-00-7	Cl	246[e]	226[e]
24704-16-3	*n*-PrO	249[g]	175[g]
	Br	252	255
	NO_2	281	262
24706-93-2	EtO	287[g]	226[g]
1819-02-9	COOEt	298[b]	203[b,e]
1962-76-1	MeO	300[b]	222[b]
1819-01-8	COOMe	343 dec[b]	262[b]
	CN	353.5	331.5

MeO-Terminated Esters



Registry no.	R	N-I temp, °C	Mp, °C
	H	173	157
	Cyclohexoxy	229	174
33905-73-6	*n*-$C_8H_{17}O$	229[f]	125[f]
33905-72-5	*n*-$C_7H_{15}O$	234[f]	127[f]
	i-BuO	236.5	155.5
40781-89-3	$EtOCH_2CH_2O$	237	127 (109.5)
33905-71-4	*n*-$C_6H_{13}O$	244[f]	125[f]
33905-70-3	*n*-$C_5H_{11}O$	253[f]	137[f]
	Me	265	199
33905-69-0	*n*-BuO	266[f]	134[f]
40781-85-9	Cl	275	196
33905-68-9	*n*-PrO	277[f]	167[f]
	Br	277	214
33905-67-8	EtO	295[f]	213[f]
	MeO	300[b]	222[b]

H-Terminated Esters



Registry no.	R	N-I temp, °C	Mp, °C
	H		207
	Me		172
	i-BuO		153.5
	$EtOCH_2CH_2O$	117	134
	n-$C_6H_{13}O$	150	119
	MeO	173	157

[a] Data from sources other than Table I are indicated by footnotes. [b] Reference 5. [c] Reference 7. [d] Compound is not nematic. Value estimated by extrapolation of N–I transition curve in binary phase diagram for this ester and the dimethoxy ester (ref 6a). [e] Reference 6a. [f] Reference 8. [g] Reference 6.

only seven do not exhibit a nematic mesophase.[11] The marked tendency of the system to be mesomorphic is particularly well shown by the three nematic compounds having only one terminal substituent. When the data in Table II are examined, trends are apparent that may be summarized as follows. Bulky, relatively nonpolar, long-chain alkoxy groups give the lowest melting points, while more compact, polar groups (CN, NO_2, COOMe, halogen, EtO MeO, Me) give the highest. The $EtOCH_2CH_2O$ substituent is about as effective as the long-chain alkoxy groups in lowering the melting point. The "abnormally" high values for MeO and H in the MeO–R and H–R series, respectively, reflect the importance of symmetry to crystalline lattice stability.

End group bulk and polarity seem to be the principal factors that influence the N–I transition temperature also. The highest values are provided by relatively compact, polar substituents (CN, COOMe, MeO). Bulky and, particularly, branched groups with little polarity give low N–I points. The effect of branching is shown by the results for isomeric alkyl moieties (cyclohexoxy < *n*-$C_6H_{13}O$, *i*-BuO < *n*-BuO). The combined effects of increasing bulk and decreasing polarity are demonstrated by the homologous series *n*-RO (Me > Et > Pr > Bu > C_5H_{11} > C_6H_{13} > C_8H_{17}) and COO-*n*-R (Me > Et > Pr > Bu). However, there appears to be a group size below which an adverse effect on mesomorphism sets in, probably because the molecule becomes too short. Thus, H and the highly polar F are well below Me and Cl in the N–I temperature order. The fact that Cl and Br give very similar values, despite the larger size and lower electronegativity of the latter, may be associated with the greater polarizability of Br.

The results are in accord with generally accepted theories of molecular structural influences on melting and N–I transition points. The melting temperature is enhanced by symmetry and strong intermolecular attractive forces. The latter are provided by polar and easily polarizable segments of the molecule. Bulky, nonpolar groups, because they inhibit close approach of neighboring molecules while contributing little or nothing to intermolecular attraction, have a lowering effect on the melting point. The same factors apply also to nematic mesophase stability except that they are conditioned by the requirement that a nematic compound must have rod-shaped molecules; *i.e.*, bulk along the longitudinal molecular axis is not nearly so deleterious as the same bulk located laterally so that it broadens the molecule. Our data for $EtOCH_2CH_2O$ appeared, at first, to be anomalous. The group is about the same size as *n*-$C_5H_{11}O$ and, presumably, more polar because of the additional ether oxygen. However, in Table II, the melting point order is *n*-$C_5H_{11}O$ > $EtOCH_2CH_2O$ and the N–I point order *n*-$C_5H_{11}O$ > *n*-$C_6H_{13}O$ > $EtOCH_2CH_2O$. For the symmetrical esters, the N–I temperature of $EtOCH_2CH_2O$ even falls below those of *n*-$C_7H_{15}O$ and *n*-$C_8H_{17}O$. This suggests that the opposing dipoles in the extended $EtOCH_2CH_2O$ group (**3**) render it less polar than a *n*-alkoxy group of similar length with its unopposed C–O–C dipole. The situation recalls the insolubility

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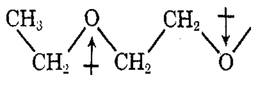
(11) In addition, 21 nematic unsymmetrical di-*n*-alkoxy esters, which are not included in Table II, have been prepared.[8]

of poly(formaldehyde) (**4**) in water, which appears to be anomalous in that poly(ethylene oxide) (**5**) is readily soluble. Superficially, **4** should be more soluble



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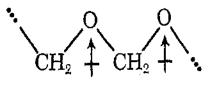

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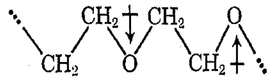

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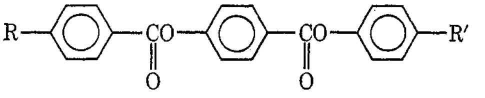
since it has the higher oxygen content. However, the C–O–C dipoles in **4** are all in the same direction, resulting in powerful intermolecular attractive forces, whereas these forces are weaker in **5** because of its alternating opposed dipoles. Individual molecules of **5** are more readily hydrated and pulled into aqueous solution from the surfaces of polymer particles. Steinsträsser's results[9] for the $EtOCH_2CH_2O$ end group in terminally substituted phenyl p-benzoyloxybenzoates (**6**) agree with ours in the **1** system. For **6**, R′ = n-Bu,



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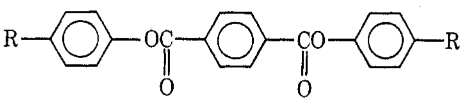
R = alkoxy, he found that the nematic ranges are R = n-$C_{10}H_{21}O$, 91–172°; R = $EtOCH_2CH_2O$, 99–170°; R = MeO, 107–235°; R = n-BuO, 113–212°; *i.e.*, the $EtOCH_2CH_2O$ ester melts well below the n-BuO ester (only 8° above the n-$C_{10}H_{21}O$ ester), and its N–I temperature is the lowest of the four. Working with Schiff bases, Dietrich and Steiger[12] have also observed nematic mesophase destabilization on replacement of $-CH_2-$ by $-O-$ in n-alkoxy substituents, and have drawn similar conclusions relating the effect to intermolecular forces.

Of the terminal substituents in Table II, long-chain alkoxy groups are most effective in lowering the melting point, while CN, NO_2, COOMe, and Br are most effective in raising it. The highest N–I temperatures are produced by CN, COOMe, MeO, and COOEt, the lowest by COOBu, cyclohexoxy, and i-BuO. Unsymmetrical di-n-alkoxy esters[8] are the lowest melting ($C_6H_{13}O$–OC_8H_{17}, mp 106°; $C_5H_{11}O$–OC_7H_{15}, mp 108°) and have the broadest nematic ranges (MeO–OBu, 134–266°; EtO–OBu, 150–270°) of the type **1** compounds that have been described to date. However, we are certain that terminal n-alkyl groups[9,12–20] and methyl[7,18,19] or chloro[20] substituents on the phenylene rings would provide still lower melting points without destroying nematic mesomorphism in consideration of data reported for other molecular systems.

It is pertinent to compare the effects of end group variation on nematic behavior in type **1** esters with those in the closely related diphenyl terephthalates (**7**) and phenyl p-benzoyloxybenzoates (**6**). Dewar



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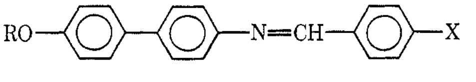
and Goldberg[6a] compared the N–I transition temperatures of five **1**–**7** ester pairs with identical end groups and found the value for the **1** ester to be invariably higher. Their explanation is that an electron-releasing end group increases the polarity of the C=O group in **1** and hence stabilizes the mesophase; there is little effect on **7**. On the other hand, an electron-withdrawing end group has little effect on **1**, but destabilizes the mesophase in **7** by reducing the polarity of the C=O group. Extension of the comparison to include five n-alkoxy end groups lends further support to this argument. The N–I temperature difference between **1** and **7** esters is 11–12° for n-$C_7H_{15}O$, n-$C_6H_{13}O$, n-BuO, and n-PrO (electron releasing), 20–23° for MeO, EtO, and Cl (electron releasing but also electron withdrawing inductively), 25° for F (strongly electron withdrawing), and 54–63° for NO_2 and COOEt (powerfully electron withdrawing in **7** since the N=O and C=O bonds are conjugated with the para oxygen, producing inordinately low N–I temperatures). Four of the type **6** esters described by Steinsträsser[9] have the same end groups (n-alkoxy) as known esters of type **1**.[8] In each of these four directly comparable pairs, the N–I transition temperature of the **1** ester is higher than that of the **6** ester. Again, this is consistent with enhancement of nematic mesophase stability by an electron-releasing end group that is in conjugation with a C=O group as suggested by Dewar and Goldberg.[6a] Both alkoxy substituents in **1** are so situated, whereas only one is in **6**. In both systems, the N–I temperature decreases with increasing end group length. The difference between N–I values for each ester pair also decreases in this order, suggesting that, as the end groups become longer, this effect becomes dominant over polarity variations in the centers of the molecules.

Correlations can also be demonstrated for type **1** esters *vs.* dissimilar systems. Dave and Dewar[21] determined the effects on nematic properties of adding nonmesomorphic para-substituted Schiff bases to p-azoxyanisole. From these data, they arranged the end groups of the Schiff bases in order of decreasing efficiency in promoting nematic mesomorphism. Gray[22] compared this order with the effects of various terminal groups (X) on the N–I transition temperatures of two homologous Schiff base systems (**8a** and **8b**).



8a, R = Me
b, R = n-$C_8H_{17}O$

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(12) H. J. Dietrich and E. L. Steiger, *Mol. Cryst. Liq. Cryst.*, **16**, 263 (1972).

(13) (a) H. Kelker and B. Scheurle, *Angew. Chem., Int. Ed. Engl.*, **8**, 884 (1969); (b) H. Kelker, B. Scheurle, R. Hatz, and W. Bartsch, *ibid.*, **9**, 962 (1970).

(14) R. Steinsträsser and L. Pohl, *Tetrahedron Lett.*, 1921 (1971).

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When the groups common to these three system, type **7** esters, and the esters in Table II are examined together (Table III), a general correspondence of the orders is evident and the agreement between systems **1** and **8a** is very good.

TABLE III
EFFICIENCIES OF END GROUPS IN PROMOTING NEMATIC MESOMORPHISM IN SYSTEMS **1**, **7**, **8a**, **8b** AND SCHIFF BASE–AZOXYANISOLE MIXTURES

System	Ref	Group efficiencies
1		MeO > NO_2 > Br ~ *n*-PrO ~ Cl > Me > *n*-$C_5H_{11}O$ > F > H
7	6a	MeO > NO_2 > Cl > *n*-$C_5H_{11}O^a$ > F > H
8a	22	MeO > NO_2 > *n*-PrO ~ Cl ~ Br > Me > *n*-$C_5H_{11}O$ > F > H
8b	22	MeO > *n*-PrO > *n*-$C_5H_{11}O$ > Me ~ NO_2^b
Mixtures	21	NO_2 > MeO > Cl = Me > Br ~ H

[a] The $C_5H_{11}O$ ester has not been reported, but this position for it is assured from interpolation between the known C_4H_9O and $C_6H_{13}O$ esters. [b] This position is questionable since the compound decomposed at the N–I transition temperature.

The use of data from a systematic structural modification study of one nematic molecular system as a guide to other systems can be rewarding. Certainly, the discovery of Kelker, *et al.*,[13a] that the *n*-butyl end group lowers the melting points of nematic Schiff bases and the demonstration by Arora, *et al.*,[7] that a methyl substituent on the central phenylene ring of type **1** esters has a similar effect have been applied to other systems with outstanding success.[9,13b,14–19] The correlations presented in this paper are further evidence that this approach is highly worthwhile.

Registry No.—**2** (R = H), 2444-19-1; **2** (R = *i*-Pr), 40782-20-5; **2** (R = *t*-Bu), 40782-21-6; **2** (R = cyclohexoxy), 40782-22-7; **2** (R = MeO), 28099-28-7; benzoyl chloride, 98-88-4; *p*-methylbenzoyl chloride, 874-60-2; *p*-methoxybenzoyl chloride, 100-07-2; *p*-isobutoxybenzoyl chloride, 40782-45-4; *p*-hexyloxybenzoyl chloride, 39649-71-3; *p*-(2-ethoxyethoxy)-benzoyl chloride, 40782-47-6; *p*-cyclohexoxybenzoyl chloride, 36823-91-3; *p*-bromobenzoyl chloride, 586-75-4; *p*-cyanobenzoyl chloride, 6068-72-0; *p*-nitrobenzoyl chloride, 122-04-3; *p*-chlorobenzoyl chloride, 122-01-0; *p*-butoxycarbonylbenzoyl chloride, 39853-28-6; *p*-*tert*-butylbenzoyl chloride, 1710-98-1; *p*-isopropylbenzoyl chloride, 21900-62-9; *p*-octyloxybenzoyl chloride, 40782-53-4; *p*-heptyloxybenzoyl chloride, 40782-54-5; *p*-fluorobenzoyl chloride, 403-43-0; *p*-propoxycarbonylbenzoyl chloride, 40782-56-7; *p*-pentyloxybenzoyl chloride, 36823-84-4; *p*-butoxybenzoyl chloride, 33863-86-4; *p*-propoxybenzoyl chloride, 40782-58-9; *p*-ethoxybenzoyl chloride, 16331-46-7; *p*-ethoxycarbonylbenzoyl chloride, 27111-45-1; *p*-methoxycarbonylbenzoyl chloride, 7377-26-6; *p*-isobutoxybenzoic acid, 30762-00-6; *p*-cyclohexoxybenzoic acid, 139-61-7; *p*-(2-ethoxyethoxy)benzoic acid, 40782-64-7; ethyl *p*-hydroxybenzoate, 120-47-8; hydroquinone, 123-31-7.

The Reversible Addition of Hydroxide to Substituted Benzaldehydes

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Received January 31, 1973

The equilibrium constants determined for the addition of hydroxide ion to a series of benzaldehydes, mono- and disubstituted in the meta and para positions, can be correlated with $\Sigma\sigma$, with a slope $\rho = 2.24$. From this the stabilization energy of the carbonyl group of benzaldehyde relative to acetaldehyde can be calculated as 2.7 kcal/mol. For benzaldehydes substituted in one ortho position a linear relationship is observed between the equilibrium constants for addition and the pK_a values of the analogous substituted benzoic acids.

Aliphatic aldehydes and some aliphatic ketones undergo a reversible hydration in neutral aqueous solutions to form the *gem*-diol.[1] Aromatic aldehydes are not hydrated to any appreciable extent, owing to the extra resonance stabilization.

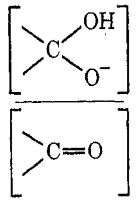
However, in basic solutions, mono- and disubstituted benzaldehydes do undergo a reversible addition of hydroxide ion to form the ionized *gem*-diol. In the present work, equilibrium constants for this addition were measured and are discussed for Scheme I, with correlations proposed for the various substituents.

Experimental Section

The substituted benzaldehydes were pure commercial products, recrystallized before use to a constant melting point. The methiodide of 4-dimethylaminobenzaldehyde, prepared by refluxing the amine with methyl iodide, had mp 158° (lit.[2] mp 156–157°).

Uv spectra were recorded on a Cary 17 spectrophotometer, and the pmr spectra on a Jeol C-60HL instrument at 30°; chemical shifts in parts per million are noted downfield relative to the sodium salt of 3-(trimethylsilyl)propanesulfonate.

The amount of hydroxide addition was followed by uv spectroscopy at 25°, by observing the instant decrease of the aromatic carbonyl band on addition of base. The spectra were recorded at various concentrations of base until the intensity decreased to a constant value, with formation of a new band. For all the benzaldehydes substituted with one or two chlorines only, the final absorption approached or was extrapolated to zero. For the unsubstituted and 2-CH_3 benzaldehydes, only 10–20% hydroxide addition was determined, and the absorption of the *gem*-diol form was taken as zero. The ratio of hydroxide adduct to carbonyl compound is shown in eq 1, where OD_0 is the carbonyl



$$\frac{\left[\,>C(OH)O^-\,\right]}{\left[\,>C{=}O\,\right]} = \frac{OD_0 - OD_{OH}}{OD_{OH} - OD_{final}} \qquad (1)$$

absorption in neutral solution and OD_{OH} is the absorption at some hydroxide concentration. These values were plotted *vs.* the hydroxide ion concentration, the slope of the line being K_{OH}, with intercepts through the origin. As shown, some of the carbonyl compounds are hydrated to a small extent in neutral solution, and OD_0 is the carbonyl absorption in the presence of of the *gem*-diol. However, the same procedure for K_{OH} is valid.

The amount of initial hydration as shown directly by nmr for 4-trimethylammonium benzaldehyde iodide and indirectly for 3-nitrobenzaldehyde (see Results and Discussion) is not more than 10%. As small amounts of *gem*-diol are difficult to deter-

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