Liquid Crystals. 6. Mesomorphic Phenols and Primary Amines. *p*-Phenylene Dibenzoates with Terminal Hydroxy and Amino Groups[1]

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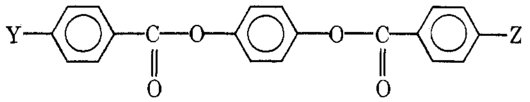
Liquid crystalline phenols and aromatic primary amines are rare, apparently because their characteristic intermolecular hydrogen bonding gives rise to melting points above the mesophase–isotropic liquid transition temperature and to nonlinear molecular associations in the liquid state. Therefore, the discovery that *p*-phenylene dibenzoates (1) with terminal OH or NH_2 groups are generally mesomorphic was unexpected. Six amines, five phenols, and the aminophenol of this molecular system were synthesized and found to exhibit nematic mesomorphism. Two of these, the diphenol and aminophenol, also form smectic mesophases. Evidence is presented to support the following explanation of this unusual behavior. Superimposed on a rigid, rod-shaped, polar molecule that is already predisposed to mesomorphism, electron donation by the terminal OH or NH_2 to the ester carbonyl with which it is conjugated produces extremely high molecular polarity. Powerful dipolar intermolecular attractive forces result, and provide a very stable mesophase when the compound melts. Within the well-ordered parallel molecular alignment of the mesophase, hydrogen bonding is no longer a detriment to mesomorphism and may, in fact, enhance it.

The molecular structural criteria for mesomorphism (liquid crystallinity)[3–6] are rigidity, rod shape, and polarity. However, most phenols and aromatic primary amines that satisfy these criteria fail to exhibit mesomorphism. An earlier communication[7] briefly described the preparation and properties of *p*-phenylene di-*p*-aminobenzoate, 1 ($Y = Z = NH_2$), and *p*-phenylene di-*p*-hydroxybenzoate, 1 (Y = Z = OH), both of which are mesomorphic, and claimed that these were the first examples of a liquid crystalline primary amine and phenol that are incapable of intramolecular hydrogen bonding. A more thorough literature search has since revealed this claim to be in error. At least two other such primary amines (2[8a] and 3[8b]) and another such phenol (4[9]) have been reported. Also, the diamine, 1 ($Y = Z = NH_2$), believed by us to be a new compound, had been described earlier in a patent[10] as an intermediate for the preparation of poly (ester imides). Nonetheless, the list is short, and it remains true that mesomorphism of these types of compounds is unusual. Gray[11] has proposed that this rarity is associated with intermolecular hydrogen bonding raising the melting point above the mesophase–isotropic liquid transition temperature, and perhaps also encouraging a nonlinear molecular arrangement that is incompatible with mesophase formation. Whatever the negative factors, it is clear that they are overcome in certain instances. Since we had discovered two examples of such behavior among the *p*-phenylene dibenzoates (1), it was decided to prepare additional phenolic and primary amino derivatives of this molecular system to see if they, too, are mesomorphic.



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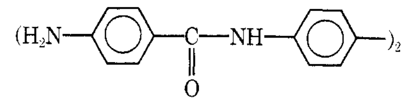

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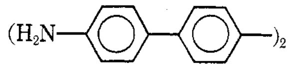

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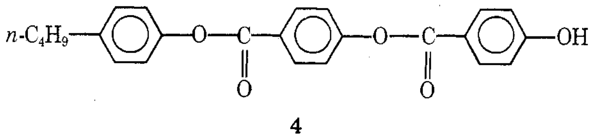

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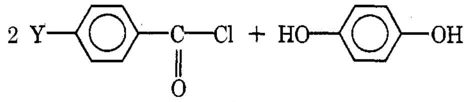
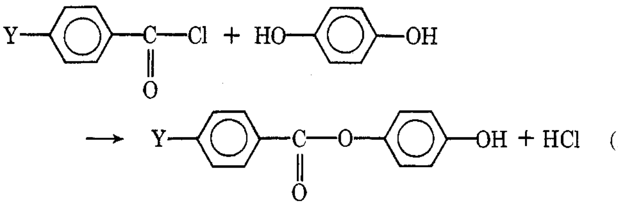
As intermediates, esters of type 1 with terminal nitro or benzyloxy groups were synthesized as in eq 1–3. The nitro groups were then reduced to NH_2 and the benzyloxy groups converted to OH by hydrogenolysis as in eq 4 and 5. The intermediates and the final products were examined with a hot stage polarizing microscope and, with only one exception, were found to be mesomorphic. These results are further evidence of the strong tendency of the *p*-phenylene dibenzoates (1) to be mesomorphic,[12] and show that, for this molecular system at least, there is little antagonism between the presence of a phenolic OH or an aromatic NH_2 group and the ability to form a mesophase.



$$\longrightarrow 1\ (Y = Z = NO_2 \text{ or } C_6H_5CH_2O) + 2HCl \quad (1)$$



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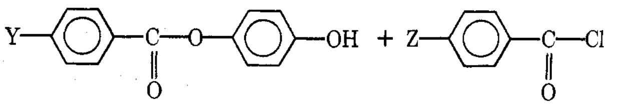
($Y = NO_2$ or $C_6H_5CH_2O$)



$$\longrightarrow 1\ (Y = NO_2 \text{ or } C_6H_5CH_2O) + HCl \quad (3)$$

$$ArNO_2 + 3H_2 \xrightarrow{Pt} ArNH_2 + 2H_2O \quad (4)$$

$$ArOCH_2C_6H_5 + H_2 \xrightarrow{Pd/C} ArOH + CH_3C_6H_5 \quad (5)$$

Experimental Section

Para-Substituted Benzoic Acids. *p*-Benzyloxybenzoic acid was obtained in 64% yield by a Williamson type reaction of ethyl *p*-hydroxybenzoate with benzyl chloride, hydrolysis of the resulting ethyl *p*-benzyloxybenzoate in ethanolic KOH solution, and acidification with HCl,[13] mp 193 °C (from ethanol).[14] The methyl, *n*-hexyloxy, and chloro acids were purchased.

Benzoyl Chlorides. Benzoyl, *p*-anisoyl, and *p*-nitrobenzoyl chlorides were commercial products. The others were obtained from the corresponding acids by treatment with thionyl chloride.

Table I. *p*-Phenylene Dibenzoates (1)[a]

Registry no.	Y	Z	Recrystn solvent	Yield, %	Transition temp, °C	
					Mp	N–I
59138-51-1	NO_2	H	Dioxane	98	231	(209)[b]
59138-52-2	NO_2	CH_3	Dioxane–ethanol	68	211	276
59138-53-3	NO_2	CH_3O	Dioxane	98	200[c]	300.5[c]
59138-54-4	NO_2	$n\text{-}C_6H_{13}O$	Ethanol	79	167	255.5[d]
59138-55-5	NO_2	Cl	Dioxane–ethanol	92	202	270
59138-56-6	NO_2	$C_6H_5CH_2O$	Dioxane–ethanol	41	211.5	284.5 dec
59138-57-7	$C_6H_5CH_2O$	H	Benzene	74	175	177
59138-58-8	$C_6H_5CH_2O$	CH_3	Benzene	95	197.5	247
59138-59-9	$C_6H_5CH_2O$	CH_3O	Dioxane	94	177.5	279.5
59138-60-2	$C_6H_5CH_2O$	$n\text{-}C_6H_{13}O$	Dioxane–ligroin	67	145	233
53201-63-1	$C_6H_5CH_2O$	$C_6H_5CH_2O$	Chloroform	72	233	260
59138-61-3	NH_2	H	Dioxane	89	239	*e*
59138-62-4	NH_2	CH_3	Dioxane	86	228.5	240
59138-63-5	NH_2	CH_3O	Dioxane	79	212.5	277.5
59138-64-6	NH_2	$n\text{-}C_6H_{13}O$	Dioxane	92	191	207
59138-65-7	NH_2	Cl	Ethanol	17	191	246
59138-66-8	NH_2	$C_6H_5CH_2O$	Dioxane–ligroin	70	221, 202.5, 174[f]	251
22095-98-3	NH_2	NH_2	Dioxane	94	323[g]	>360 dec
59138-67-9	OH	H	Dioxane	95	258	>355 dec
59138-68-0	OH	CH_3	Dioxane–ligroin	94	220.5	>355 dec
59138-69-1	OH	CH_3O	Dioxane	97	219	>355 dec
59138-70-4	OH	$n\text{-}C_6H_{13}O$	Ethanol–water	18	175	>310 dec
59138-71-5	OH	NH_2	Dioxane	83	304.5	>308[h]
53201-62-0	OH	OH	Dioxane	66	328 dec[i]	>360[h]

[a] Satisfactory analytical data (±0.4% for C, H, N for the amines, and Cl for the chloroamine) were reported for all new compounds listed in the table. [b] Monotropic transition observed on supercooling the isotropic melt. [c] Lit.[19] values: mp 200.2 °C, N–I transition temperature 300.2 °C. [d] There is also a Sm–N transition at 210 °C. [e] Not mesomorphic. [f] Polymorphic. [g] Lit.[10] mp 310 °C. [h] A focal-conic texture, indicating smectic mesomorphism, develops at varying temperatures on cooling the melt. The maximum temperature at which its appearance has been noted is ca. 300 °C. In other determinations, it was observed to appear (and to disappear again on heating) at much lower temperatures. [i] This melting point was reported earlier[7] to be 340 °C, but has been found to vary with heating rate. The 328 °C figure is an average from five determinations, and is in good agreement with the differential scanning calorimeter value of 327 °C at a heating rate of 20 °C/min.

***p*-Hydroxyphenyl Benzoates.** *p*-Hydroxyphenyl *p*-nitrobenzoate was prepared in 57% yield by overnight reaction of *p*-nitrobenzoyl chloride (practical grade) and a fivefold molar excess of hydroquinone in pyridine solution at room temperature,[15] followed by precipitation in water,[12] mp 199 °C (from ethanol) (lit.[16] 193.5 °C). Anal. Calcd for $C_{13}H_9NO_5$: C, 60.24; H, 3.50. Found: C, 60.14; H, 3.50.

p-Hydroxyphenyl *p*-benzyloxybenzoate was obtained in 64% yield by the same general procedure, but with *p*-benzyloxybenzoyl chloride and at reflux temperature. Reaction at room temperature gave a yield of only 21% and purification of the product was difficult, mp 210 °C (from ethanol). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 74.88; H, 4.95.

***p*-Phenylene Dibenzoates with Terminal Nitro and Benzyloxy Groups.** The general procedure for the preparation of *p*-hydroxyphenyl benzoates was used for synthesis of these compounds also. The symmetrically substituted esters, 1 ($Y = Z = NO_2$) and 1 ($Y = Z = C_6H_5CH_2O$), were obtained from the appropriate acyl chloride and hydroquinone. The former, a known compound,[10,12,17] was produced in good yield at room temperature. However, the latter required reaction at reflux, reflecting the low reactivity of *p*-benzyloxybenzoyl chloride (see previous paragraph).

Unsymmetrically substituted esters were prepared from ArCOCl and *p*-hydroxyphenyl *p*-benzyloxybenzoate or *p*-nitrobenzoate. Here again, a difference in reactivity was observed. The nitrophenol reactions proceeded satisfactorily at room temperature, whereas the benzyloxyphenol required refluxing. The ester, 1 ($Y = NO_2$; $Z = C_6H_5CH_2O$), could have been made either from unreactive benzyloxyphenol and nitrobenzoyl chloride or from unreactive benzyloxybenzoyl chloride and nitrophenol. This dismal choice was decided by the better availability of the nitrophenol at the time.

The esterifications were run overnight or longer, and 1.5–3 mol of ArCOCl per mole of phenolic OH was used. A high molar ratio improves yields, but also encourages the formation of by-product acid anhydride during the aqueous precipitation step.[18,19] E.g., *p*-benzyloxybenzoyl chloride (18.0 mmol) and *p*-hydroxyphenyl *p*-nitrobenzoate (6.00 mmol) in 60 ml of dry pyridine (room temperature, 42 h) gave 2.47 mmol (41%) of the desired ester, 1 ($Y = C_6H_5CH_2O$; $Z = NO_2$). In addition, there were recovered 4.04 mmol of *p*-benzyloxybenzoic acid, mp 193, 187.5 °C (by acidification of the aqueous pyridine filtrate), and 5.50 mmol of *p*-benzyloxybenzoic anhydride, mp 117 °C (lit.[20] 119 °C), ir (KBr) 1760 and 1719 (C=O doublet), 1057 cm^{-1} (C–O–C stretch) (from recrystallization of the crude ester). We have not found anhydride by-products to be a serious problem since they are more soluble than the esters and, therefore, are easily removed by recrystallization.

Further results are summarized in Tables I and II.

Table II. Infrared Spectra of *p*-Phenylene Dibenzoates (1)[a]

Y	Z	Absorption bands, cm^{-1}	
		C=O stretch	N–H or O–H stretch
CH_3O	CH_3O	1723	
$C_6H_5CH_2O$	$n\text{-}C_6H_{13}O$	1730	
Cl	NO_2	1735	
NH_2	NH_2	1703	3480, 3433, 3380, 3360
NH_2	H	1699, 1732	3479, 3380
NH_2	CH_3	1701, 1733	3476, 3378
NH_2	CH_3O	1710–1730[b]	3462, 3438, 3374
NH_2	$n\text{-}C_6H_{13}O$	1698, 1728	3477, 3379
NH_2	$C_6H_5CH_2O$	1697, 1730	3458, 3364
NH_2	Cl	1702, 1738	3472, 3374
OH	NH_2	1700–1710[b]	3382
OH	OH	1700	3390
OH	H	1710, 1733	3438
OH	CH_3	1712, 1731	3420–3440[b]
OH	CH_3O	1710, 1728	3420
OH	$n\text{-}C_6H_{13}O$	1702, 1732	3421

[a] KBr pellet. [b] Broad band.

***p*-Phenylene Dibenzoates with Terminal Amino Groups.** These were obtained by low pressure hydrogenation of the corresponding nitro esters over platinum catalyst in dioxane. Typically, 7 mmol of the nitro compound, 300 ml of dioxane that had been recently distilled from sodium metal, 0.2 g of PtO_2, and an initial H_2 pressure of 25 psig were used. The mixture was shaken at room temperature until the theoretical pressure drop occurred, and the product was recovered by filtration, distillation of dioxane from the filtrate, and recrystallization of the residue from an appropriate solvent.

In the preparation of 1 ($Y = Z = NH_2$), neither the starting dinitro ester nor the product was completely soluble in the dioxane, but the reaction proceeded smoothly. The insoluble portion of the product was separated from catalyst by extraction with hot dioxane.

Two of the reductions gave by-products that were difficult to separate from the desired amines. Both appear to have been the result of incomplete hydrogenation. In the synthesis of 1 ($Y = Cl$; $Z = NH_2$), the material was a solid with a metallic lustre that was insoluble in all common solvents. We have identified it as di-*p*-(*p*-chlorobenzoyloxy)phenyl *p*-azoxybenzoate (**5**): mp 315.5 °C; nematic–isotropic (N–I) transition temperature >322 °C dec (from aniline); ir (KBr) 1735 (ester C=O), 1303 (N–O in –N=NO–), 1089 cm^{-1} (ArCl). Anal. Calcd for $C_{40}H_{24}N_2O_9Cl_2$: C, 64.27; H, 3.24; N, 3.75; Cl, 9.49. Found: C, 64.25; H, 3.14; N, 3.78; Cl, 9.41. Hydrolysis in ethanolic KOH followed by acidification gave *p*-chlorobenzoic acid, mp 240.5 °C (after two vacuum sublimations) (lit. 239.7,[21] 241.5 °C[22]), and another acid that was insoluble in common organic solvents with the exception of pyridine, did not melt at 380 °C but gave an orange sublimate at ca. 280 °C. This behavior is consistent with the reported properties of *p*-azoxybenzoic acid.[23] In the preparation of 1 ($Y = C_6H_5CH_2O$; $Z = NH_2$), the by-product was also a relatively insoluble solid, mp 256 °C, N–I transition temperature >308 °C dec (from nitrobenzene). The compound has not been identified, but there is evidence that it, too, contains an unreduced N–O bond (C, H, and N contents are below those of the amine and the yield of by-product decreases with increasing hydrogenation time).

Other results are presented in Tables I and II.

***p*-Phenylene Dibenzoates with Terminal Hydroxy Groups.** The phenolic esters were synthesized by low pressure hydrogenolysis of the corresponding benzyloxy compound over a palladium catalyst in dioxane.[24,25] For a typical run, 2 mmol of the benzyloxy ester, 300 ml of dioxane (freshly distilled from sodium), 0.3 g of 5% Pd on charcoal, and an initial H_2 pressure of 25 psig were used. The mixture was shaken at room temperature overnight and worked up as described above for hydrogenations of nitro esters. The only hydrogenolysis that did not go well was that of 1 ($Y = C_6H_5CH_2O$; $Z = n\text{-}C_6H_{13}O$), which apparently contained a catalyst-poisoning contaminant. Three runs, with spent catalyst removed and fresh catalyst added each time, served only to improve the quality of recovered starting material. The fourth run gave a low (18%) yield of the desired phenol.

1 ($Y = Z = OH$) was first prepared by tetrazotization of 1 ($Y = Z = NH_2$) followed by hydrolysis.[7] This method was abandoned when it was found that extensive hydrolysis of ester linkages occurs as a side reaction. The hydroquinone produced in the hydrolysis complexes with the desired phenolic ester. The 1:1 complex with 1 ($Y = Z = OH$) was isolated as rod-shaped plates: mp 249.5 °C; ir (KBr) 3470 and 3390 (aromatic OH), 3080 and 3050 (aromatic C–H), 1713 cm^{-1} (ester C=O). Anal. Calcd for $C_{26}H_{20}O_8$: C, 67.82; H, 4.38. Found: C, 67.71; H, 4.28. On heating the material above its melting point, there was heavy sublimation, leaving a residue of crude 1 ($Y = Z = OH$), mp 313.5 °C (to nematic liquid), appearance of focal-conic smectic texture at 235 °C.

Demethylation of 1 ($Y = Z = OCH_3$) with BBr_3, $AlCl_3$, or $AlBr_3$ was also explored. The first two reagents gave low-melting solids that were not mesomorphic, while $AlBr_3$ gave very poor yields of a solid: mp 333 °C; N–I transition temperature >339 °C; crystallization temperature 212 °C; ir (KBr) 3395 (aromatic OH), 2930 (aliphatic C–H), 1700 cm^{-1} (ester C=O). This product resembles 1 ($Y = Z = OH$) in melting behavior except that it does not display a smectic mesophase. The ir spectrum indicates that Friedel–Crafts ring methylation occurred via the CH_3Br formed in the ether cleavage and the $AlBr_3$.

The remaining results are summarized in Tables I and II.

Apparatus. Transition temperatures were determined with a Reichert Thermopan polarizing microscope equipped with a Kofler micro hot stage. Calorimetric measurements were taken with a Perkin-Elmer differential scanning calorimeter, Model DSC-1 B. Both instruments were calibrated against pure substances having known melting points. Ir spectra were measured on a Perkin-Elmer grating ir spectrophotometer, Model 457. Hydrogenations and hydrogenolyses were run in a Parr Series 3910 hydrogenation apparatus.

Analyses. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

For the most part, the syntheses of the amines and phenols went well. In the preparation of the intermediate nitro- and benzyloxy-substituted type **1** esters by reaction of an aroyl chloride and a phenol in pyridine solution (eq 1–3), it was found that a benzyloxy group on either the acid chloride or the phenol has a deactivating effect. For these compounds, good yields were obtained only by operating at reflux, whereas their nitro-substituted counterparts reacted readily at room temperature. High molar ratios of acid chloride to phenol gave improved yields, but also resulted in anhydride formation during precipitation of the reaction mixtures in water (eq 6 and 7). The anhydrides were easily removed from the desired esters by recrystallization. All of the intermediate esters are mesomorphic (Table I).

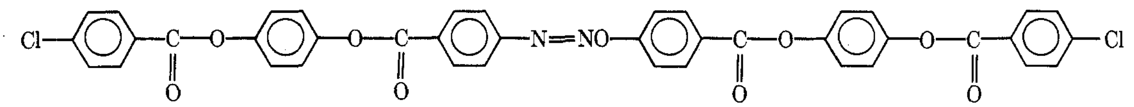
$$\mathrm{ArCOCl} + \mathrm{H_2O} \xrightarrow{\text{pyridine}} \mathrm{ArCOOH} + \mathrm{HCl} \qquad (6)$$

$$\mathrm{ArCOCl} + \mathrm{ArCOOH} \xrightarrow{\text{pyridine}} \mathrm{(ArCO)_2O} + \mathrm{HCl} \qquad (7)$$

The reductions of nitro esters to amino esters with hydrogen over platinum catalyst (eq 4) went smoothly with the exception of the reaction leading to 1 ($Y = NH_2$; $Z = Cl$), which gave a low yield (17%) because of great difficulty in separating a by-product that proved to be the azoxy compound **5**. An incompletely reduced by-product (unidentified) was also formed in smaller amount during the synthesis of 1 ($Y = C_6H_5CH_2O$; $Z = NH_2$). Catalyst selectivity was displayed in this synthesis, too, in that 1 ($Y = C_6H_5CH_2O$; $Z = NO_2$) was reduced to the amine in 70% yield with no apparent hydrogenolysis of the benzyloxy group.

The hydrogenolyses of benzyloxy-substituted esters to phenols over palladium on charcoal (eq 5) proceeded nicely, again with one exception. The ester 1 ($Y = C_6H_5CH_2O$; $Z = n\text{-}C_6H_{13}O$) stoutly resisted repeated attempts at hydrogenolysis, but finally gave a low yield of phenol on the fourth try.

Of the seven amines, five phenols, and the "hybrid" aminophenol, 1 ($Y = OH$; $Z = NH_2$), that were prepared, only 1 ($Y = NH_2$; $Z = H$) failed to exhibit mesomorphism (Table I). Furthermore, the relatively high N–I transition temperatures of the liquid crystalline amines and phenols show that their nematic mesophases are very stable. This is particularly noteworthy for the diamine and the phenols, the mesophases of which decompose thermally at temperatures over 300 °C without undergoing transition to isotropic liquid. If one uses the N–I point as a measure of "group efficiency" in promoting nematic mesomorphism in system 1,[12,19] the OH end group is unsurpassed and NH_2 is exceeded by only a few others. E.g., for 1 ($Y = CH_3O$; $Z =$ variable), the N–I transition temperatures for various Z's decrease in the order $OH > CN > CH_3O \simeq NO_2 > NH_2 \simeq Cl \simeq Br > CH_3 > F > CF_3 > H$. The heat of transition is a still better criterion for mesophase stability since it is a direct measure of the energy required to disrupt the ordered nematic molecular "lattice". Dewar and Griffin[19] have determined N–I transition enthalpies for esters of the type 1 ($Y = CH_3O$; $Z =$ variable). From these data, they calculated $\Delta S_{N\text{-}I}$ and found a correlation between the ΔH and ΔS values which implies that molecular order in the nematic mesophase is closely related to the strength of intermolecular association for this series. Unfortunately, we could not determine $\Delta H_{N\text{-}I}$ for the hydroxy ester because it decomposes before the transition temperature is reached. However, the amino ester, 1 ($Y = CH_3O$; $Z = NH_2$), gave $\Delta H_{N\text{-}I} = 0.324$ kcal/mol, from which was calculated $\Delta S_{N\text{-}I} = 0.589$ eu. These values place NH_2 relative to other Z groups as follows: $\Delta H_{N\text{-}I}$ CH_3O, 0.408 > CH_3, 0.387 > NH_2, 0.324 > Cl, 0.282 > Br, 0.248 > F, 0.244 > CN, 0.228 > NO_2, 0.192 > H, 0.158; $\Delta S_{N\text{-}I}$



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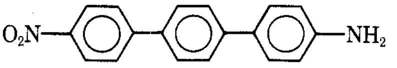
CH_3, 0.713 > CH_3O, 0.711 > NH_2, 0.589 > Cl, 0.511 > F, 0.466 > Br, 0.451 > CN, 0.383 > H, 0.355 > NO_2, 0.334. Presumably, OH would occupy a position no lower than that of NH_2 in both lists. Again, these results indicate that NH_2 (and, by inference, OH) as an end group in 1 produces highly stable, well-ordered nematic mesophases.

Since mesomorphic primary amines and phenols are rare, we sought an explanation of why system 1 is so apparently well suited to produce them. Gray's proposal[11] (mentioned in the introduction) that intermolecular H bonding is responsible for their scarcity is reasonable and has experimental support. Listed below on the left are a primary amine and several phenols that do not exhibit mesomorphism. Opposite them, on the right, are closely related mesomorphic compounds in which intermolecular H bonding through NH_2 or OH has been reduced by the opportunity for intramolecular H bonding (**9** and **10**), by substitution of aliphatic OH for phenolic OH (**11**), or has been eliminated completely by etherification of phenolic OH (**12** and **13**).

Not mesomorphic



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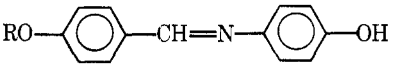

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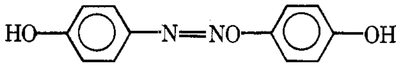

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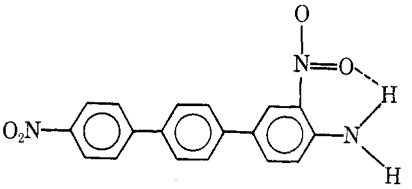
Mesomorphic



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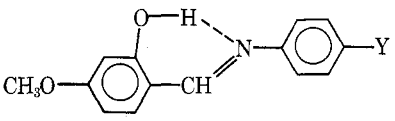

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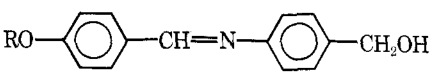
(Y = CN, Ph, $CH{=}CH_2$, n-C_4H_9)



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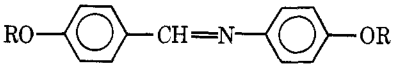
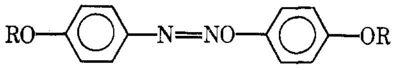


(ref 30)

12



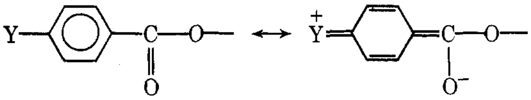
(ref 30 and 31)

13

($R = CH_3$, C_2H_5, and n-alkyl)

The N–H and O–H stretch bands from the ir spectra of the amines and phenols of this study are presented in Table II. For the amines, with the exception of the aminophenol 1 (Y = OH; Z = NH_2), there are free (not H bonded) NH_2 bands in the 3430–3480-cm^{-1} region, but no evidence of free OH (3590–3650 cm^{-1}) in the phenols. Bands at 3360–3380 cm^{-1} for N–H and at 3380–3440 cm^{-1} for O–H show that there is H bonding in all of the compounds. It seems safe to assume that this is intermolecular in light of the high melting points (Table I) and because an extended conformation of the ester molecules, precluding intramolecular H bonding, is the only one consistent with the observed mesomorphism. Thus, if Gray's hypothesis is correct, as it appears to be, amines and phenols of type 1 must possess some special feature or features whereby they exhibit mesomorphism in spite of intermolecular H bonding.

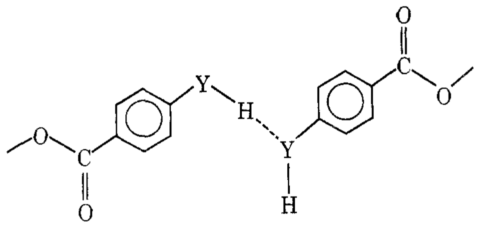
The three rigid, polarizable phenylene rings are undoubtedly helpful, this group having been clearly demonstrated to encourage mesomorphism,[32] as are the two carbonyl groups with their dipoles crosswise to the long molecular axis, providing lateral intermolecular attractive forces.[33] However, the most important special feature appears to be conjugation of the terminal OH or NH_2 group with C=O through the intervening phenylene ring. Returning to the ir spectral data in Table II, the C=O stretch band frequencies conform very well with the views of Dewar et al. concerning the effects of end groups on this bond in system 1.[17,19] Their suggestion is that an electron-releasing end group conjugated with the ester carbonyl results in a significant contribution by structure **14**, whereas an electron-withdrawing group has little effect on C=O. If this is correct, there should be a shift in the carbonyl absorption band to lower frequency on replacement of an electron-withdrawing by an electron-releasing end group owing to the decreased double bond character of the C–O bond. This is exactly what we observed. Starting with the electron-withdrawing end groups, Cl and NO_2, and proceeding to the moderately electron-releasing alkoxy substituents, the



14

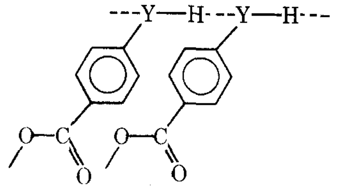
band shifts from 1735 cm^{-1} to 1723–1730 cm^{-1}. For the more potent electron releasers, NH_2 and OH, the band is shifted to 1703 and 1700 cm^{-1}, respectively, in the spectra of the diamino and dihydroxy esters. For unsymmetrically substituted amines and phenols, two C═O absorption bands were usually observed, reflecting the individual effects of the dissimilar end groups on the carbonyls nearest them. Arranging these data in descending order of absorption frequency in cm^{-1}, the groups fall into the same sequence of electron-withdrawing > moderately electron-releasing > strongly electron-releasing: Cl 1738; H, CH_3 1731–1733; alkoxy 1728–1732; OH 1702–1712; NH_2 1697–1710. The polar contributing structure **14** should enhance intermolecular attraction and thus encourage mesomorphism. Since there appears to be a large contribution by **14** for the amines and phenols, their liquid crystallinity is no longer so surprising. However, the benign role of H bonding and the smectic mesomorphism observed for two of the esters remain to be explained.

The ir spectra, high melting points, and molecular structures of the amines and phenols all indicate intermolecular H bonding, and yet these compounds exhibit very stable mesophases. Accordingly, we must conclude that H bonding is not a deterrent to mesomorphism here and, in consideration of the very high mesophase stabilities, may even encourage it. We propose that this unusual behavior is associated with the particularly strong tendency of the rod-shaped molecules in this series to assume a well-ordered parallel alignment as a result of powerful lateral dipole–dipole attractive forces. These, *in turn, we ascribe to the large contribution of the polar* structure **14** to the resonance hybrid. Under these circumstances, with the molecules already in a parallel array, there is no obvious reason why end-to-end H bonding (**15**) should not occur. The resulting linear dimers (or polymers in the cases of the diamine, diphenol, and aminophenol) would not only be compatible with nematic mesomorphism, but would be expected to enhance mesophase stability by providing additional intermolecular attraction.[34]



15 (Y = NH or O)

By a similar argument, sidewise H bonding (**16**) in a preexisting parallel molecular "lattice" is also reasonable, and would encourage smectic mesomorphism by providing additional lateral intermolecular attraction[34] and by lining molecules up in a layered arrangement. We believe it is significant that **1** (Y = Z = OH) and **1** (Y = OH; Z = NH_2) are the only amino or phenolic esters that display a focal-conic texture, indicating smectic liquid crystallinity. The structures of these two esters are particularly favorable for sidewise H bonding, being capable of association at both molecular termini. (The diamine has the requisite structure, too, but NH_2 hydrogen bonds less readily than phenolic OH.) It is pertinent also that a ring-methylated version of **1** (Y = Z = OH) is not smectic (see Experimental Section), which can be explained by lateral methyl substituents preventing close enough approach of adjoining parallel molecules to allow sidewise H bonding.



16 (Y = NH or O)

When viewed with crossed polarizers, the initial melts of both **1** (Y = Z = OH) and **1** (Y = OH; Z = NH_2) display birefringent schlieren-textured or striated zones in a pseudoisotropic matrix that flashes brightly on mechanical disturbance, indicating that it is nematic. On cooling, there is a partial transition to focal-conic texture which, although reversible, occurs at varying temperatures and is not detected as a phase change by the differential scanning calorimeter. For both melts, the flashing nematic and focal-conic smectic textures coexist well below the temperature at which the focal-conic birefringence first appears. These data suggest that the melts are partly nematic and partly smectic, with the proportion of the latter gradually increasing on cooling. This is closely analogous to the cybotactic nematic mesophases proposed by de Vries,[35] for which he postulates a combination of classical nematic molecular organization and more highly ordered bundles of molecules. The presence of both end-to-end (**15**) and sidewise (**16**) H bonds would account for the dual nematic–smectic nature of the mesophases, and interchange between these modes of H bonding is consistent with a gradual transition from nematic to smectic predominance on cooling. X-ray diffraction studies of the melts are indicated to test this hypothesis.

Looking at the other known examples of mesomorphic primary amines and phenols that are incapable of intramolecular H bonding in terms of the above discussion, it is seen that they, too, have special structural features that compensate for the usually deleterious effects of intermolecular H bonding on liquid crystallinity. Compounds **2** and **4** have the same features as the amines and phenols of this paper (phenylene rings, carbonyl groups, NH_2 or OH in conjugation with C═O) with **2** having the added advantage of the increased rigidity and extra phenylene ring provided by the biphenylene linkage. Compound **3** has the highly rigid, rod-shaped tetraphenylene ring system which is probably polarized to a considerable extent by electron donation from the NH_2 groups. In summary, there is evidence that phenolic and aromatic primary amino derivatives subject to intermolecular H bonding are mesomorphic only if they satisfy to an unusually high degree the structural criteria for liquid crystallinity.

Acknowledgment. We are grateful to Dr. Joseph A. Dilts for performing the differential scanning calorimeter experiments, and for helpful discussions concerning interpretation of the results.

Registry No.—**1** (Y = Z = CH_3O), 1962-76-1; **1** (Y = Z = OH) hydroquinone, 59138-72-6; **5**, 59138-73-7; hydroquinone, 123-31-9; *p*-benzyloxybenzoyl chloride, 1486-50-6; *p*-hydroxyphenyl *p*-benzyloxybenzoate, 59138-74-8; *p*-hydroxyphenyl *p*-nitrobenzoate, 13245-55-1; benzyloxyphenol, 103-16-2; nitrobenzoyl chloride, 122-04-3; nitrophenol, 100-02-7; *p*-benzyloxybenzoic acid, 1486-51-7; *p*-benzyloxybenzoic anhydride, 1486-49-3; benzoyl chloride, 98-88-4; *p*-methylbenzoyl chloride, 874-60-2; *p*-methoxybenzoyl chloride, 100-07-2; *p*-hexyloxybenzoyl chloride, 39649-71-3; *p*-chlorobenzoyl chloride, 122-01-0.

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Intramolecular Diels–Alder Reactions. 10. Syntheses and Cyclizations of Some *N*-(Cinnamyl and phenylpropargyl)cinnamamides and Phenylpropiolamides[1a]

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The nine possible unsaturated amides $Ph(C_2)CH_2NHC(=O)(C_2)'Ph$, where (C_2) and $(C_2)'$ are variously *cis*-CH=CH–, *trans*-CH=CH–, and –C≡C– groups, were synthesized. Diynic amide **6** underwent intramolecular Diels–Alder reaction in refluxing Ac_2O to form a mixture of benz[*f*]isoindoles **15a** (from cyclization in mode 1) and **16a** (from cyclization in mode 2). Under these same conditions *trans,trans*-dienic amide **8** did not cyclize, while four other amides gave cyclization in only one mode (for each) to form hydro derivatives of **15a** and **16a**. Modal selectivity in the cyclizations is interpreted in terms of relative frontier molecular orbital energy levels for the various substrate molecules.

In a series of preceding papers from this laboratory[2–6] we presented the syntheses and intramolecular Diels–Alder reactions (by means of refluxing acetic anhydride) of unsaturated esters of the $Ar(C_2)CH_2OC(=O)(C_2)'Ar'$ type, where Ar and Ar′ are phenyl or substituted phenyl groups and (C_2) and $(C_2)'$ are variously –C≡C–, *cis*-CH=CH–, and *trans*-CH=CH– groups. Of the nine possible combinations for (C_2) and $(C_2)'$ only five types have thus far been synthesized, and just three of these types have been found susceptible to intramolecular Diels–Alder reaction. Successful cyclizations led to the formation of cyclolignan lactones, compounds which bear the skeletal structure of 4- (or 9-) arylnaphtho[2,3-*c*]furan-1(3*H*)-one. An extension of these studies to the syntheses and cyclizations of the analogous amides $Ph(C_2)CH_2NRC(=O)(C_2)'Ph$, where R = H or benzyl, is underway in our laboratory. Studies on four *N*-benzyl amides have already been reported,[7] while the present paper describes the syntheses of all nine possible parent amides (R = H) and studies on cyclizations of six of them. Cyclization of a seventh parent amide will be considered in a subsequent paper.[8]

Used in the syntheses of the unsaturated amides were the hydrochloride salts of *trans*-cinnamylamine (**1**),[9] phenylpropargylamine (**2**), and *cis*-cinnamylamine (**3**). Amine salt **2** was obtained in 79% overall yield by Gabriel synthesis from phenylpropargyl chloride.[10] Low-pressure catalytic hydrogenation of **2** in the presence of $Pd–BaSO_4$–quinoline gave nearly a quantitative yield of **3**. Schotten–Baumann condensations between these amine salts and the freshly prepared acid chlorides from phenylpropiolic acid, *trans*-cinnamic acid, and *cis*-cinnamic acid produced the nine crystalline amides **4–12**, in yields of 57–81% (Table I). *N*-(*cis*-Cinnamyl)-*trans*-cinnamamide (**7**) was also obtained (55%) by hydrogenation of *N*-(phenylpropargyl)-*trans*-cinnamamide (**9**) in the presence of Lindlar catalyst plus quinoline.

Of special interest in the syntheses of **10–12** is the handling of *cis*-cinnamic acid. Saponification of ethyl *cis*-cinnamate[11] gave *cis*-cinnamic acid, which could be stored in dry benzene at 0–10 °C in the dark for several months without isomerization. Just before use, the acid was converted into its sodium salt by means of sodium hydride, and then into *cis*-cinnamoyl chloride (in high isomeric purity) by means of thionyl chloride.

Identities of the amides were checked by ultraviolet, ^1H NMR, and infrared spectra (as well as by elemental analyses). In particular, absorption bands were found for N–H stretching at ca. 3440 cm^{-1} (weak) and for the carbonyl moiety of an N-substituted amide at 1650–1670 cm^{-1} (strong) in all compounds.[12a] Bands for the trans-disubstituted alkene linkage[12b] at ca. 970 cm^{-1} and for the triple bond in the acid moiety[12c] at 2220 cm^{-1} were also appropriately observed.