7 hr. The reaction mixture was concentrated *in vacuo*, and the residue was neutralized with sodium bicarbonate and extracted with chloroform. The chloroform extract was dried over anhydrous magnesium sulfate and evaporated. The residual oil was chromatographed on alumina with ethyl acetate and 0.2 g. of II and 0.1 g. of the mixture of XIIIa and XIIIb in a ratio of about 3:1, m.p. 138–140° (from benzene–petroleum ether), were obtained.

Rearrangement of VI. A.—A solution of 0.5 g. of VI and 1.5 ml. of triethylamine in 2.0 ml. of formic acid was heated at 160° for 6 hr. The reaction mixture was concentrated *in vacuo*, water was added to the residue, and the separated crystals were extracted with chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and evaporated to give 0.4 g. of yellow crystals, which were found to be identical with V by comparison of their infrared spectra.

B.—A solution of 0.5 g. of VI and 0.6 ml. of concentrated hydrochloric acid in 30 ml. of ethanol was refluxed for 37 hr. The reaction mixture was concentrated *in vacuo*, and the residue was neutralized with sodium bicarbonate and extracted with ethyl acetate. The ethyl acetate extract was dried over anhydrous magnesium sulfate and evaporated to give 0.4 g. of residual crystals, which were found to be identical with V.

2-Anilino-5-ethoxycarbonyl-6H-1,3-thiazine (XV).—To a solution of 0.58 g. of XII in 10 ml. of methanol, 0.4 g. of aniline was added and refluxed for 1.5 hr. The reaction mixture was concentrated *in vacuo* and the residue was extracted with ether. Evaporation of ether left a crystalline residue, which was recrystallized from benzene–petroleum ether to give 0.43 g. (61%) of pale brown needles: m.p. 121–123°; λ_{max}^{EtOH} 311 mμ (log ε 4.34); n.m.r., τ 6.38 (C-6 H, singlet), 0.97 (NH, broad).

Anal. Calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68; S, 12.22. Found: C, 59.45; H, 5.51; N, 10.66; S, 12.46.

5-Ethoxycarbonyl-1-phenyl-2-thio-1,2,3,4-tetrahydropyrimidine (XVI).—To the solution of 0.2 g. of 5-ethoxycarbonyl-2-oxo-1-phenyl-1,2,3,4-tetrahydropyrimidine[3] in 3.0 ml. of absolute pyridine, 0.2 g. of phosphorus pentasulfide was added and refluxed for 3.5 hr. The reaction mixture was concentrated *in vacuo*, and water was added to the residue which was then extracted with chloroform. The chloroform extract was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by chromatography on alumina and 0.05 g. of pale yellow needles, m.p. 192°, was obtained: λ_{max}^{EtOH} 315 mμ (log ε 4.13).

Anal. Calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.53; H, 5.38; N, 10.68; S, 12.20. Found: C, 59.45; H, 5.55; N, 10.74; S, 12.20.

Rearrangement of XV.—A solution of 0.6 g. of XV in 1.2 ml. of 50% formic acid was heated on the steam bath for 8 hr. Water was added to the reaction mixture which was then extracted with ethyl acetate.

The ethyl acetate extract was dried over anhydrous magnesium sulfate and evaporated. The residual oil was chromatographed on alumina with ethyl acetate and the following products were obtained: 0.03 g. of N-phenylthiourea; 0.051 g. of pale yellow needles, m.p. 192°, which was found to be identical with XVI obtained above; 0.07 g. of II; and 0.017 g. of pale yellow needles (XVII) of m.p. 175–178°, λ_{max} 316 mμ (log ε 4.17).

Anal. Calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.53; H, 5.38; N, 10.68; S, 12.20. Found: C, 58.99; H, 5.26; N, 10.13; S, 12.21.

Acknowledgment.—The authors express their deep gratitude to Professors M. Tomita and S. Uyeo of Kyoto University, and to Dr. K. Takeda, Director of this laboratory, for their encouragement, and to Professor S. Nagakura of the University of Tokyo for his helpful discussion. Thanks are also due to the members of physicochemical section of this laboratory for infrared, ultraviolet, and n.m.r. spectral measurements, to the members of the analytical section of this laboratory for elemental analyses, and to Mr. T. Ishiba for his technical assistance.

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p-Alkoxy- and *p*-Carbalkoxybenzoates of Diphenols. A New Series of Liquid Crystalline Compounds[1]

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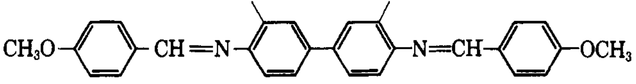
Nineteen liquid crystalline *p*-phenylene and *p,p'*-biphenylene esters of *p*-alkoxy- and *p*-carbalkoxybenzoic acids have been synthesized. Ten of them exhibit very broad mesomorphic ranges and high (mesophase → liquid) transition temperatures. The effects of structural changes on phase transitions in this series are discussed. Four new *n*-alkyl terephthalates were also prepared in the course of this work.

Since we plan a general survey of the use of liquid crystals[2] as solvents, we have been concerned with the choice of suitable materials for this work. Any unusual solvent properties of such compounds should be greater, the greater the anisotropic ordering of the molecules in them. This in turn should be greater, the stronger the anisotropic forces between the molecules and the lower the temperature. Now strong anisotropic forces should be reflected in a high transition temperature from nematic[2] to normal liquid; clearly what we need is a compound with a high transition temperature and a long mesomorphic range. The molecular orientation in such a compound should be particularly strong at the lower end of its mesomorphic range, near the melting point.

We had a further interest in compounds of this type in view of their possible use as stationary phases in gas chromatography. Our preliminary work[3] was carried out with compounds that had short mesomorphic ranges and low transition temperatures to normal liquid; the range of materials that could be separated on such columns is clearly limited.

One series of compounds has been described that appeared to meet our specifications, the 4,4'-bis(*p*-methoxybenzylideneamino)biphenyls; the 3,3'-dichloro derivative (I) in particular is stated[4] to be nematic



I

from 149 to above 340°. However, when we examined this substance, we found it to be thermally unstable,

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(1) This work was supported by grants from The National Science Foundation and The Robert A. Welch Foundation.

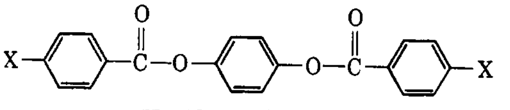
(2) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press Inc., New York, N. Y., 1962.

(3) M. J. S. Dewar and J. P. Schroeder, *J. Am. Chem. Soc.*, **86**, 5235 (1964).

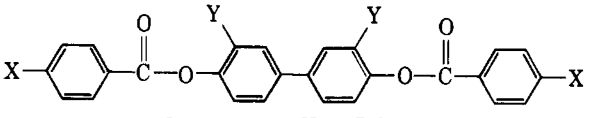
(4) C. Wiegand, *Z. Naturforsch.*, **6b**, 240 (1951).

even at temperatures close to its melting point; Schiff bases of this type would in any case be unsuitable for many of our purposes in view of the chemical reactivity of the C=N groups in them. We therefore decided to see if we could obtain analogous but more stable materials by replacing the C=N linkages with other more suitable groups.

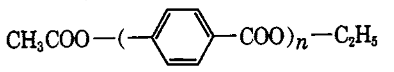
An obvious choice seemed to be the ester group, -COO-. Aromatic esters are known to be thermally stable and relatively resistant to hydrolysis; moreover, the favored conformation of a compound such as phenyl benzoate should be one in which the aryl groups are coplanar and *trans* to one another, just as they are in the corresponding Schiff base. Compounds such as II or III should therefore possess all the features (linear shape, terminal alkoxy groups, polar internal groups interspersed with aromatic rings) that are known[2] to favor the mesomorphic state. Moreover, Vorländer[5] has reported that the analogous unsymmetrical esters (IV) are mesomorphic over wide temperature ranges and have high (nematic → liquid) transition temperatures; it seemed likely that II and III would combine their desirable properties with greater accessibility.



IIa, X = RO–
b, X = ROOC–



IIIa, Y = H; X = RO–
b, Y = H; X = ROOC–
c, Y = Cl; X = RO–
d, Y = Cl; X = ROOC–



IV

This paper describes the preparation and properties of nineteen esters of types II and III. All proved to be mesomorphic and the majority possess the desired combination of a long liquid crystalline range and high (mesophase → liquid) transition temperature. Wide variation of X made it possible to observe the effects of structural changes on mesomorphic behavior in a system which had not been studied previously.

These compounds were prepared from an excess of the appropriate *para*-substituted benzoyl chloride and the diphenol in pyridine. The requisite *p*-carbalkoxybenzoic acids were made by partial esterification of terephthaloyl dichloride followed by hydrolysis. The di-*n*-alkyl terephthalates were obtained as readily isolable by-products. The *p*-alkoxybenzoic acids were prepared by reaction of the appropriate alkyl bromide with ethyl *p*-hydroxybenzoate to give the ethyl *p*-alkoxybenzoate, which was saponified. The acids were converted to the corresponding acid chlorides with thionyl chloride.

Experimental

Starting Materials.—These were commercial products except for 3,3'-dichloro-4,4'-dihydroxybiphenyl which was prepared by chlorination of 4,4'-dihydroxybiphenyl in glacial acetic acid with the stoichiometric amount of chlorine.[6] After recrystallization from water, the product melted at 130–131.5° (lit.[6] m.p. 124°).

Mono-*n*-alkyl Terephthalates.—One molar equivalent of the 1-alkanol dissolved in benzene was added to a refluxing benzene solution of terephthaloyl dichloride over a period of 1–3 hr. Refluxing was continued for 1 hr. after the addition to complete the reaction.

p-Carbomethoxybenzoyl chloride, b.p. 108–110° (0.5 mm.), lit.[7] b.p. 135–138° (10 mm.), and *p*-carbethoxybenzoyl chloride, b.p. 102–105° (0.4 mm.), lit.[7] b.p. 133–134° (6 mm.), were obtained in 50% yield directly from the reactions with methanol and ethanol, respectively, by fractional distillation. Both products contained small amounts of unreacted terephthaloyl dichloride which caused trouble in the next step (esterification) by forming polymers which were difficult to remove from the desired products. Accordingly, the higher homologs were not distilled. Instead, the reaction mixture was hydrolyzed by addition of pyridine and water, the benzene was evaporated, and the residue was washed with hydrochloric acid to remove excess pyridine and pyridine hydrochloride. Acidic materials were separated from by-product dialkyl terephthalate by extraction with aqueous sodium carbonate solution[8] and recovered from the extract by precipitation with hydrochloric acid. After drying, the precipitate was taken up in chloroform and filtered to remove terephthalic acid. Evaporation of the filtrate gave the desired monoester.

Table I lists physical and analytical data for the mono-*n*-alkyl terephthalates, including the methyl and ethyl esters which were prepared as derivatives of the corresponding acid chlorides, and for the di-*n*-alkyl terephthalates recovered from the base-insoluble residues by ether extraction.

***p*-Alkoxybenzoic Acids.**—The ethyl *p*-alkoxybenzoates were prepared in 92–93% yield from ethyl *p*-hydroxybenzoate and the appropriate alkyl bromide by a method adapted from Gray and Jones.[9] The esters were saponified in ethanolic potassium hydroxide (95–100% yields). The resulting *p*-alkoxybenzoic acids exhibited the following phase transitions: *p*-*n*-butyloxybenzoic acid, (solid → nematic) 149°, (nematic → liquid) 162° (lit.[10] 147°, 160°); *p*-*n*-hexyloxybenzoic acid, (solid → nematic) 108°, (nematic → liquid) 153° (lit.[10] 105°, 153°); *p*-*n*-heptyloxybenzoic acid, (solid → smectic) 92°, (smectic → nematic) 99°, (nematic → liquid) 148° (lit.[10] 92°, 98°, 146°).

***para*-Substituted Benzoyl Chlorides.**—With the exceptions of *p*-anisoyl chloride, which was purchased, and the *p*-carbomethoxy- and *p*-carbethoxybenzoyl chlorides (*cf.* above), the acid chlorides were prepared from the acids by treatment with thionyl chloride in the presence of a catalytic amount of pyridine. The excess thionyl chloride was distilled to give the acid chloride as a residue product.

Phenylene and Biphenylene Esters of *p*-Alkoxy- and *p*-Carbalkoxybenzoic Acids.—Typically, 0.018 mole of the *para*-substituted benzoyl chloride was dispersed in dry pyridine (30 ml.) and a solution of 0.006 mole of the diphenol in 30 ml. of dry pyridine added with swirling. The mixture was allowed to stand overnight at room temperature. If the product precipitated, it was filtered, washed successively with pyridine, water, and ethanol, and dried.

If the ester did not precipitate (or did so in poor yield), the reaction mixture was acidified with dilute hydrochloric acid, and the insoluble solid was recovered by filtration. After washing with water, the wet solid was stirred for 1 hr. in 300 ml. of 5% aqueous Na_2CO_3 solution, and the insoluble ester was filtered off, washed with water, and dried. The excess acid was precipitated from the filtrate with hydrochloric acid and recovered.

The ester was recrystallized from a suitable solvent. The properties of the pure products are presented in Table II.

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(5) D. Vorländer, *Z. physik. Chem.* (Leipzig), **105**, 211 (1923).

(6) J. C. Cain, *J. Chem. Soc.*, **85**, 7 (1904).

(7) J. L. R. Williams, T. M. Laakso, K. R. Dunham, D. G. Borden, J. Van den Berghe, J. A. Van Allan, and D. D. Reynolds, *J. Org. Chem.*, **25**, 817 (1960).

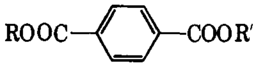
(8) In one instance (mono-*n*-decyl terephthalate), the sodium salt was insoluble in aqueous Na_2CO_3 but dissolved on washing with hot water.

(9) G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).

(10) G. W. Gray and B. Jones, *ibid.*, 4179 (1953).

TABLE I

MONO- AND DI-*n*-ALKYL TEREPHTHALATES



R	R′	Yield,[a] %	Recrystn. solvent	M.p., °C. Obsd.	M.p., °C. Lit.	%C Calcd.	%C Found	%H Calcd.	%H Found	Neut. equiv. Calcd.	Neut. equiv. Found
CH_3	H	...	Benzene	223	230[b]						
C_2H_5	H	...	Benzene	170	171[b]						
n-C_3H_7	H	18	None	129	129[c]						
n-C_4H_9	H	15[d]	None	135	133.5[b]						
n-C_5H_{11}	H	30	Petr. ether (60–68°)	120		66.1	66.1	6.8	7.0	236	236
n-C_6H_{13}	H	36	Petr. ether (60–68°)	112		67.2	67.3	7.25	7.5	250	253
n-$C_{10}H_{21}$	H	36	Ethanol	113		70.6	70.6	8.55	8.8	306	317
CH_3	CH_3	...[e]	Aq. ethanol	141	142[f]						
n-C_3H_7	n-C_3H_7	64	Ethanol	30	31[g]						
n-C_4H_9	n-C_4H_9	38[d]	Ethanol	20	16[h]						
n-C_5H_{11}	n-C_5H_{11}	38	Ethanol	22		70.6	70.8	8.55	8.6		
n-C_6H_{13}	n-C_6H_{13}	24	Ethanol	36	37[i]						
n-$C_{10}H_{21}$	n-$C_{10}H_{21}$	32	Ethanol	58	57[j]						

[a] Based on the alcohol. [b] Ref. 7. [c] J. B. Cohen and H. S. de Pennington, *J. Chem. Soc.*, **113,** 62 (1918). [d] Some material was lost mechanically in working up this run. [e] A small amount of this codistilled with the *p*-carbomethoxybenzoyl chloride and was recovered in the next step. [f] N. Zelinsky and N. Glinka, *Ber.*, **44,** 2305 (1911). [g] J. Berger, *ibid.*, **10,** 1742 (1877). [h] M. Pfannl, *Monatsh.*, **32,** 509 (1911). [i] H. Staudinger, A. Steinhofer, and R. C. Bauer, *Ann.*, **517,** 54 (1935). [j] R. N. Miller, J. O. Crooke, and E. G. Rietz, *J. Am. Chem. Soc.*, **74,** 4214 (1952).

TABLE II

LIQUID CRYSTALLINE *p*-PHENYLENE AND *p,p′*-BIPHENYLENE ESTERS OF *p*-ALKOXY- AND *p*-CARBALKOXYBENZOIC ACIDS

Type	R	Recrystn. solvent	Yield, %	Smectic range, °C.	Nematic range, °C.	%C Calcd.	%C Found	%H Calcd.	%H Found
IIa	CH_3	Dioxane	70	...	222–300[a]	69.8	69.9	4.8	4.85
	n-C_4H_9	C_2H_5OAc	40	(141)[b]	156–253	72.7	72.8	6.5	6.6
	n-C_6H_{13}	Petr. ether	85	111–120	120–205	74.1	74.25	7.4	7.3
	n-C_7H_{15}	Petr. ether	44	83–125	125–206	74.7	74.6	7.75	7.7
IIb	CH_3	Dioxane	53	...	262–343d[c]	66.4	66.3	4.2	4.3
	C_2H_5	C_2H_5OAc	70	(180)[b]	203–298	67.5	67.2	4.8	4.9
	n-C_3H_7		79	(140)[b]	193–219	68.6	68.45	5.3	5.1
	n-C_4H_9		79	(131)[b]	139–155	69.5	69.5	5.8	6.0
	n-C_5H_{11}	Petr. ether	78	123–133	133–146	70.3	70.4	6.3	6.2
	n-C_6H_{13}	Petr. ether	58	129–135	135–142	71.1	70.9	6.7	6.7
	n-$C_{10}H_{21}$	Ethanol	9	133–137	137–145	73.4	73.3	7.9	8.0
IIIa	CH_3	Dioxane	88	...	251–366d[c]	74.0	74.1	4.9	4.9
	n-C_4H_9	C_2H_5OAc	93	171–184	184–358d[c]	75.8	75.6	6.4	6.4
	n-C_6H_{13}		90	153–181	181–330	76.7	76.8	7.1	7.1
	n-C_7H_{15}		62	150–211	211–316	77.1	77.4	7.45	7.65
IIIb	n-C_6H_{13}	C_2H_5OAc	..[d]	164–270	270–295	73.8	74.0	6.5	6.2
	n-$C_{10}H_{21}$	Dioxane	85	160–240	240–251	75.6	75.5	7.7	7.7
IIIc	CH_3	Dioxane	72	...	220–349d	64.3	64.1	3.85	4.2[e]
IIId	n-$C_{10}H_{21}$	C_2H_5OAc	56	158–163	...	69.3	69.1	6.8	6.9[f]

[a] K. Nakazawa, S. Matsuura, and S. Baba [*J. Pharm. Soc. Japan*, **74,** 498 (1954)] report that this compound melts at 212°. [b] Monotropic (nematic → smectic) transition at this temperature. [c] Nematic phase decomposes before transition to isotropic liquid. [d] This compound was not obtained pure by the ordinary procedure. Its synthesis is described in the Experimental part. [e] *Anal.* Calcd: Cl, 13.55. Found: Cl, 13.3 [f] *Anal.* Calcd: Cl, 8.5. Found: Cl, 8.6.

The ester IIId (R = n-$C_{10}H_{21}$) showed a marked tendency to gel and would not crystallize from a variety of solvents. It was purified by several reprecipitations from ethyl acetate, one of which was preceded by treatment with Norit.

Attempts to prepare pure IIIb (R = n-C_6H_{13}) by the above procedure were unsuccessful. Recrystallization of the crude product from ethanol gave a 27% yield of impure ester (low carbon content). Concentration of the mother liquor gave a 31% yield of *n*-hexyl 4-(4-hydroxyphenyl)phenyl terephthalate (V)

Anal. Calcd. for $C_{26}H_{26}O_5$: C, 74.6; H, 6.3; mol. wt., 418. Found: C, 74.55; H, 6.4; mol. wt. (Rast method), 412.

The infrared spectrum was consistent with the proposed structure, showing characteristic phenolic absorptions at 2.9, 8.2, and 8.5 μ which were absent or very weak in the spectrum of the completely esterified product. The phenol displayed no liquid crystalline behavior, melting at 189–190° after recrystallization from carbon tetrachloride.

Treatment of this compound with 5 molar equiv. of *p*-carbo-*n*-hexyloxybenzoyl chloride in pyridine gave a 70% yield of the desired ester, the properties of which are listed in Table II.

Melting Points.—Transition temperatures were determined with a Nalge–Axelrod melting point apparatus which has a viewing microscope and provision for observing birefringence.

Analyses.—Four of the compounds were analyzed at The University of Texas, the remainder by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Discussion

Our object in this work was to synthesize stable liquid crystalline materials with long mesomorphic ranges and high transition temperatures to normal liquids; this was achieved. Of the nineteen new esters, ten have mesomorphic ranges greater than 90°; among these the lowest (mesophase → liquid) transition point is 205°. Particularly interesting compounds are of type IIIa where R is n-C_4H_9, n-C_6H_{13}, and n-C_7H_{15}. These have mesomorphic ranges of 166

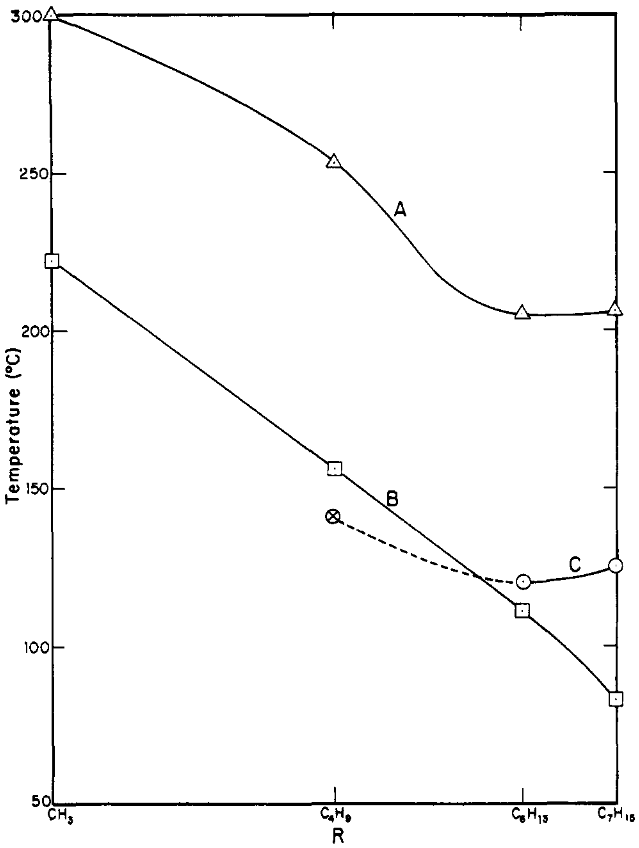


Figure 1.—Phase transition temperatures for the system RO-phenylene (IIa): curve A (—△—), (nematic → liquid); curve B (—□—), (solid → mesophase); curve C (—○—), (smectic → nematic); monotropic transitions are designated by the symbol ⊗.

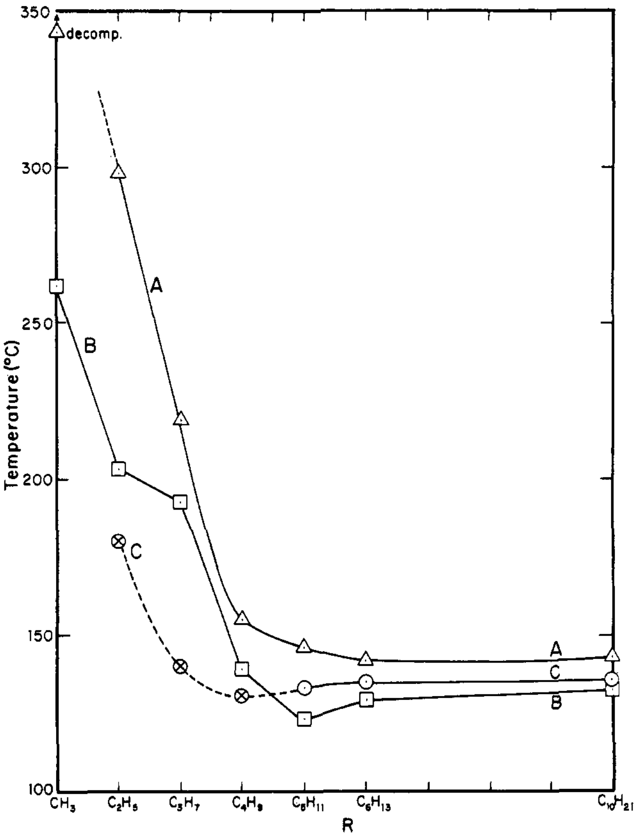
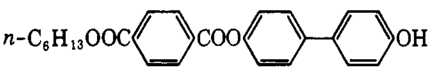


Figure 2.—Phase transition temperatures for the system ROOC-phenylene (IIb): curve A (—△—), (nematic → liquid); curve B (—□—), (solid → mesophase); curve C (—○—), (smectic → nematic); monotropic transitions are designated by the symbol ⊗.

to more than 187° and (nematic → liquid) transition temperatures of 316 to >358°. Investigation of their performance as solvents is in progress.

The ester yields were generally good. A notable exception is IIb (R = *n*-$C_{10}H_{21}$) which was obtained in only 9% yield. This seems strange, for the same acid chloride gave good results with both 4,4′-dihydroxybiphenyl and its 3,3′-dichloro derivative.

Another low-yield reaction was that of *p*-carbo-*n*-hexyloxybenzoyl chloride and 4,4′-dihydroxybiphenyl. Only 27% of the desired ester was isolated and this could not be satisfactorily purified The main product (31% yield) was the half-esterified compound V. Treatment of this with a large excess of the acid chloride in pyridine gave a 70% yield of the desired ester. Although the latter is mesomorphic over a wide temperature range (131°), V is not liquid crystalline at all, supporting Gray's statement that phenolic compounds are unable to display mesomorphism because of intermolecular hydrogen bonding.[2] V was the only half-esterified product observed in this work.



V

Since this is a new series of liquid crystalline compounds, it is of interest to consider the effects of structural variations on phase transitions. In Figures 1–3 transition temperatures are plotted against length of alkyl substituent (R) with the arylene part of the structure held constant.

The (nematic → liquid) transition point decreases regularly with increasing alkyl chain length up to C_6H_{13} for both the RO- and ROOC-phenylene series (Figures 1 and 2). However, in the corresponding biphenylene series (Figure 3 and Table II), the transition temperature is still decreasing at the longest R which was studied ($C_{10}H_{21}OOC$– and $C_7H_{15}O$–).

These results are reasonable and in accord with previous observations on other nematic systems. Increased alkyl chain length reduces the rod-shaped molecule's rigidity and thus its ability to fit readily into the parallel molecular arrangement of the nematic phase. The result is decreased mesophase stability and a lower transition temperature. The disrupting effect of the alkyl substituent does not appear to increase with length beyond *n*-hexyl when the central aromatic group is phenylene. However, it does when the latter is biphenylene, because the more rigid biphenylene moiety produces a higher order of stability and consequently higher transition temperatures. Under these circumstances even very long alkyl groups would be expected to be relatively mobile and their disrupting effect indeed continues to increase with chain length beyond C_6H_{13}.

In the ROOC- and RO-phenylene series, no smectic phase was observed when R = CH_3 and only monotropic (nematic → smectic) transitions[11] up through R = C_4H_9. Note that the monotropic and enantiotropic (reversible) transition temperatures fall on the same smooth curve in Figures 1 and 2, illustrating the

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[11] *I.e.*, observed only on cooling the nematic phase.

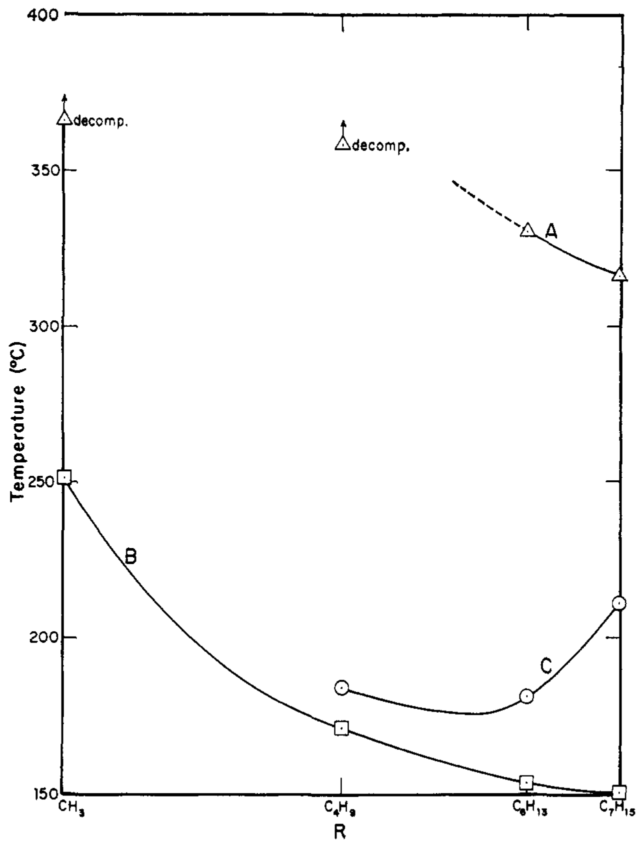

Figure 3.—Phase transition temperatures for the system RO–biphenylene (IIIa): curve A (—Δ—), (nematic → liquid); curve B (—□—), (solid → mesophase); curve C (—○—), (smectic → nematic).

fact that a monotropic transition simply means that the smectic phase is not stable above the melting point of the compound and is therefore observed only if the nematic phase can be supercooled sufficiently. With increasing alkyl chain length, the (smectic → nematic) transition point decreases up to C_4H_9 for the ROOC–phenylene series, to C_6H_{13} for the RO–phenylene and RO–biphenylene series, and then rises slightly. It continues to decrease through $C_{10}H_{21}$ for the ROOC–biphenylene series (Table II). No smectic phase was observed for R = CH_3 in the RO–biphenylene series and the (smectic → nematic) transitions for R = C_4H_9 and longer are enantiotropic.

Formation of a smectic phase requires not only parallel alignment of rod-shaped molecules but also weak end-to-end intermolecular attraction so that the layers of the laminar structure are free to slide by one another. The relatively small methyl group furnishes poor "insulation" against strong terminal attractions which preclude a smectic phase. As the size of the alkyl group increases, these forces decrease while lateral intermolecular attraction (between the polymethylene chains) is added and a smectic phase appears. Usually the (smectic → nematic) transition temperature curve *rises* steeply initially as this increasing lateral attraction resists the movement of molecules from one layer to another, thus favoring a smectic structure.[2] The initial *drop* in the curves for the present system is highly unusual. However it is well known[2] that an opposing effect occurs—namely, an increasing tendency for interpenetration of the layers as the terminal alkyl chains grow longer and more flexible. It is surprising that a system in which this effect obviously predominates has not been encountered before. The rise in the latter portions of the curves can be explained by the other, ordinarily predominant, effect.

In the normal pattern for liquid crystalline compounds, the melting points (solid → mesophase transitions) in the ROOC–phenylene series display an irregular downward trend with increasing alkyl chain length, leveling off after C_5H_{11}. However, *two* smooth curves can be drawn through the points if they are divided according to whether the number of carbon atoms in R is even or odd. In both RO– series, the transition temperatures decrease regularly, almost linearly, with increasing length of R. One can speculate that the reason for these unusually regular variations is a similarity between the crystal lattices of the solids and the molecular arrangements in the mesophases to which they melt. If this were true, the (solid → mesophase) transitions would closely resemble (mesophase → mesophase) transitions which invariably give smooth plots.[2]

Turning now to the effects of the central aromatic group, replacement of phenylene by biphenylene raises all transition temperatures, (nematic → liquid) the most, (smectic → nematic) less, and the melting point least of all. Thus, biphenylene broadens both the smectic and nematic ranges. This is not surprising in view of the greater molecular rigidity and polarizability of the biphenyl group.

It had been hoped that the 3,3′-dichloro-4,4′-biphenylene group would give still broader mesophase ranges as it does in the 4,4′-di(4-methoxybenzylideneamino)biphenyl system. However, its effect was not great in the methoxy-substituted ester and it almost eliminated liquid crystallinity in the *n*-decyl ester. The latter compound also gelled readily in a variety of solvents. Apparently, the large chlorine substituents weaken the lateral intermolecular attractions in the decyl ester, reducing the mesomorphic range from 91 to only 5° and facilitating solvation.

As expected, solubility in nonpolar solvents increases with increasing alkyl chain length and decreases when phenylene is replaced by biphenylene.