Effects of Central and Terminal Groups on Nematic Mesophase Stability[1]

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Sixteen liquid crystalline *p*-phenylene esters of hydroquinone and *para*-substituted phenyl esters of terephthalic acid have been synthesized. Most of them exhibit very broad nematic ranges and high transition temperatures. The effects of structural changes on mesophase stability are also discussed.

Since nematic liquid crystals[2] are being used as solvents for nmr,[3] esr,[4] uv,[5] and gas chromatography[6,7] studies, there is a need for suitable mesomorphic substances with wide mesomorphic temperature ranges and favorable glass-forming tendencies. We were also interested in the effect of changing the central and terminal groups in a mesomorphic molecule on the stability of its nematic mesophase.

One way of getting wider nematic ranges is to mix two miscible mesomorphic components with approximately the same mesophase–isotropic transition points. In most cases the solid–mesophase transition point is lowered, while the mesophase–isotropic point varies only slightly. The *p*-phenylene esters of the *p*-alkoxybenzoic acids (I)[8] were suitable for both our purposes since they exhibit long mesophases and since the terminal and central groups can be easily modified. We have accordingly made a number of new compounds of this type and studied their ability to form mesophases, both alone and as mixtures with I. The modifications made were inversion of the carboxylate groups in I, giving II, and substitution of various terminal groups in place of alkoxyl.

Experimental Section

***para*-Substituted Benzoic Acids.**—Ethyl *p*-hydroxybenzoate was converted to ethyl *p*-alkoxybenzoate with the appropriate alkyl halide, and the esters were saponified to the corresponding acids by the method of Gray and Jones.[9] The transition points agreed well with those of Gray and Jones. The *p*-fluoro-, *p*-nitro-, and *p*-chlorobenzoic acids were obtained commercially and the *p*-carbethoxybenzoic acid was obtained from Dr. J. P. Schroeder, University of North Carolina at Greensboro. The preparation of the 1,4-bicyclo[2.2.2]octylene esters of *p*-*n*-hexyloxy- (III) and *p*-*n*-octyloxy- (IV) benzoic acids and the *trans*-1,4-cyclohexylene ester of *p*-*n*-hexyloxybenzoic acid (V) have been reported elsewhere.[10]

***para*-Substituted Benzoyl Chlorides.**—The acid chlorides were prepared from the acids by treatment with thionyl chloride. The excess thionyl chloride was flashed off to give, as the residue, the acid chloride.

***p*-Phenylene Esters of *para*-Substituted Benzoic Acids (I).**—Typically, a solution of hydroquinone (0.03 *m*) and dry pyridine (50 ml) was added to a solution of dry pyridine (50 ml) and *p*-alkoxybenzoyl chloride (0.09 *m*). The mixture was stirred at room temperature for 24 hr and then acidified with dilute hydrochloric acid. The precipitate was filtered off, washed with water, and slurried for 4 hr in 500 ml of 5% sodium bicarbonate solution. The solution was then filtered and the solid ester was recrystallized from a suitable solvent. The properties of the pure products are presented in Table I.

***para*-Substituted Phenols.**—The *p*-*n*-hexyl- and *n*-heptylphenols were prepared by the method of Klarmann, *et al.*[11] The two synthesized phenols exhibited the following melting points: *p*-*n*-hexyloxyphenol, mp 46–48° (lit.[10] 48°); *p*-*n*-heptyloxyphenol, mp 52–58° (lit.[10] 60°). All other *p*-alkoxyphenols and *p*-fluoro-, *p*-nitro-, *p*-chloro-, and *p*-carbethoxyphenols were obtained commercially.

***para*-Substituted Phenyl Esters of Terephthalic Acid (II).**—Typically, a solution of *p*-alkoxyphenol (0.042 *m*), terephthaloyl dichloride (0.014 *m*), and 100 ml of dry pyridine were stirred for 24 hr at room temperature. The solution was then acidified with dilute hydrochloric acid, and the precipitate was filtered off, washed with ethanol, and recrystallized from a suitable solvent. The properties of the pure products are presented in Table II.

Phase Diagrams.—Mixtures of the two components in known proportions were prepared by fusion and rapid cooling. The transition temperatures of the sample were then obtained both with a polarizing microscope and with a capillary melting point apparatus. The transitions reported are the temperatures at which solid or mesophase have completely disappeared. In the phase diagrams, ⊡ denotes the solid → nematic transition and ⊙ denotes the nematic → isotropic transition. The results are tabulated in Table III.

Melting Points.—Transition temperatures were determined both with a Thomas–Hoover capillary melting point apparatus and with a Leitz Ortholux II polarizing microscope fitted with a heating stage. All melting points are corrected.

Analyses.—Elemental microanalyses were performed by Alfred Bernhardt Microanalytical Laboratories and Galbraith Laboratories.

Results and Discussion

The *p*-phenylene esters of the *para*-substituted benzoic acids provide an excellent system for the study of structural effects on mesophase stability because they are so versatile. We have already used[10] this system to study the role of benzene rings on mesophase stability, and we have now extended these investigations to the role of the terminal groups and the effect of inverting the central carboxyls.

Two homologous series of esters were prepared, *i.e.*, the *p*-phenylene bis-*p*-alkoxybenzoates (I with X = *n*-alkoxy) and the di-*p*-alkoxyphenyl terephthalates (II with X = *n*-alkoxy). All these compounds showed nematic mesophases;[12] the nematic → liquid transition

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[1] This work was supported by the U. S. Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

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

[3] G. R. Luckhurst, *Quart. Rev. Chem. Soc.*, **22**, 179 (1968); A. Saupe and G. Englert, *Phys. Rev. Lett.*, **11**, 462 (1963); L. C. Snyder and E. W. Anderson, *J. Amer. Chem. Soc.*, **86**, 5023 (1964); J. C. Rowell, W. D. Phillips, L. R. Melby, and M. Panar, *J. Chem. Phys.* **43**, 3442 (1965).

[4] S. H. Glarum and J. H. Marshall, *ibid.*, **46**, 55 (1967); A. Carrington and G. R. Luckhurst, *Mol. Phys.*, **8**, 401 (1964).

[5] E. Sackmann, S. Meiboom, and L. C. Snyder, *J. Amer. Chem. Soc.*, **90**, 3567 (1968).

[6] (a) M. J. S. Dewar and J. P. Schroeder, *ibid.*, **86**, 5235 (1964); (b) *J. Org. Chem.*, **30**, 3485 (1965).

[7] H. Kelker, *Z. Anal. Chem.*, **198**, 254 (1963).

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

[9] G. W. Gray and B. Jones, *J. Chem. Soc.*, 4179 (1953).

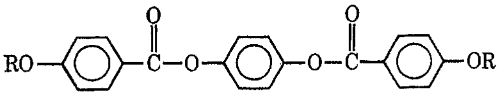
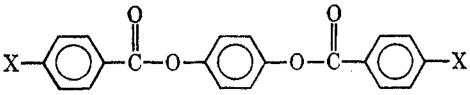
[10] M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

[11] E. Klarmann, L. W. Gatyas, and V. A. Shternov, *ibid.*, **54**, 298 (1932).

[12] We saw no indication of smectic phases under the polarizing microscope; however, Dr. J. L. Fergson has told us that he has detected enantiotropic smectic–nematic transitions in Ig and Ih, and monotropic one in If, using DTA. Since our primary concern was with the stabilities of nematic mesophases and, since DTA equipment is not available here, we are reporting our results in their original form. Since the smectic–nematic transition in If is monotropic, it seems very unlikely that any of the lower esters show stable smectic phases.

TABLE I

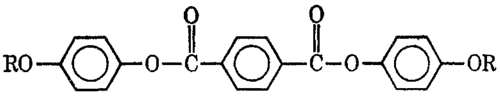
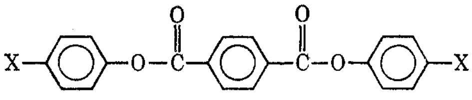
LIQUID CRYSTALLINE *p*-PHENYLENE ESTERS OF *para*-SUBSTITUTED BENZOIC ACIDS

Compd no.	R or X	Recrystn solvent	Yield, %	Mp, °C	Nematic → liquid transition, °C	% C Calcd	% C Found	% H Calcd	% H Found
A. 									
Ia	CH_3	Dioxane	80	213[a,b]	297[c]	69.84	69.90	4.79	4.85
Ib	C_2H_5	EtOAc	33	226	287	70.93	70.75	5.46	5.46
Ic	n-C_3H_7	EtOAc	47.2	175	249	71.87	71.51	6.03	6.11
Id	n-C_4H_9	EtOAc	57	153[d]	241[e]	72.71	72.44	6.54	6.53
Ie	n-C_6H_{13}	Hexane	63	121.5[f]	211	74.10	74.18	7.39	7.48
If	n-C_7H_{15}	Hexane	55	121	198[f]	74.70	74.91	7.74	7.82
Ig	n-C_8H_{17}	Hexane	63.9	118	192	75.23	75.15	8.07	8.09
Ih	n-$C_{10}H_{21}$	Hexane	48.7	122	178	76.15	76.30	8.62	8.63
B. 									
Ii	Cl	EtOAc	65.9	226	246	62.04	61.79	3.12	3.02
Ij	CO_2Et	EtOAc	48.0	203	242	67.53	67.37	4.80	4.92
Ik	NO_2	Dioxane	67.5	260	266	58.83	58.62	2.96	3.12
Il	F	EtOAc	68.3	210[g]		67.80	67.89	3.39	3.60

[a] Obtained from Dr. J. P. Schroeder, University of North Carolina at Greensboro. [b] Lit. 222,[8] 212° [K. Nakazawa, S. Matsuura, and S. Baba, *J. Pharm. Soc. Jap.*, **74**, 498 (1954)]. [c] Lit.[8] 300°. [d] Lit.[8] 156°. [e] Lit.[8] 253°. [f] Dr. J. P. Schroeder has confirmed these values which differ from those of ref 8. [g] No mesophase.

TABLE II

LIQUID CRYSTALLINE *para*-SUBSTITUTED PHENYL ESTERS OF TEREPHTHALIC ACIDS

Compd no.	R or X	Recrystn solvent	Yield, %	Mp, °C	Nematic → liquid transition, °C	% C Calcd	% C Found	% H Calcd	% H Found
A. 									
IIa	CH_3	Dioxane	57.5	205	277	69.84	69.70	4.79	4.74
IIb	C_2H_5	EtOAc	62.3	216	266.5	70.93	71.02	5.46	5.58
IIc	n-C_3H_7	EtOAc	70.0	198	238	71.87	72.08	6.03	6.17
IId	n-C_4H_9	EtOAc	58.6	183	229	72.71	72.51	6.54	6.61
IIe	n-C_6H_{13}	EtOAc	52.7	161	201	74.10	73.94	7.39	7.31
IIf	n-C_7H_{15}	EtOAc	49.0	153	188	74.70	74.58	7.74	7.63
B. 									
IIg	Cl	EtOAc	69.0	195	226	62.04	62.28	3.12	3.17
IIh	CO_2Et	EtOAc	85.6	191	235	67.53	67.65	4.80	4.72
IIi	NO_2	DMSO-H_2O	39.4	242[a]		58.83	58.76	2.96	3.05
IIj	F	EtOAc	57.5	226[b]		67.80	67.77	3.39	3.54

[a] Monotropic nematic mesophase at 227°. [b] No mesophase.

temperatures are plotted as a function of chain length in Figures 1 and 2. It will be seen that in each case the points lie on two different curves, one for alkyl groups with an even number of carbon atoms, the other for those with an odd number. In each case the curve for even alkyl groups is the higher, and the curves for the *p*-phenylene esters (I) both lie higher than the corresponding ones for the *p*-alkoxyphenyl terephthalates (II), implying that for each pair of analogs the isomer I forms the more stable mesophase.

As the alkyl chain in a compound of this type is lengthened, the stability of the nematic mesophase should be affected in at least four different ways.[13] First, the alkyl group will act as a diluent, increasing the mean separation between molecules and so likewise the separation between them; this will in turn reduce the anisotropy of the intermolecular forces and so make the mesophase less stable. Secondly, the increase in size of the polar terminal groups will likewise reduce the attractions between them. Thirdly, the increase in length of the molecule will lead to an increase in its geometrical anisotropy. Fourthly, the overall polar-

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(13) G. W. Gray, *Mol. Cryst.*, **1**, 33 (1966).

Table III

Solid–Mesophase (Top) and Nematic–Isotropic (Bottom) Temperatures for Binary Systems[a]

Components		Mol %, component A											Eutectic	
A	B	0	10	20	30	40	50	60	70	80	90	100	Mol % of A	Temp, °C
Ia	IIa	205	203	199	195	190	188	196	201	205	211	213	47.3	184
		277	279	281	283	285	287	289	291	293	295	297		286
Ib	IIb	216	213	210	205	200	196	205	212	218	223	226	48.0	194
		266.5	268.5	270.5	272.5	274.5	276.5	279	281	283	285	287		276
Ic	IIc	198	196	192	185	177	167	159	163	167	171	173.5	56.9	157
		238	239	240	241	242	243	244	245	246	247	248		244
Id	IId	183	181	178	175	172	165	155	144	145	152	153	73.8	137
		229	230	231.5	233	234	235	236	237	238.5	240	241		238
Ie	IIe	161	159	156	152	147	141	135	126	117	119	121.5	84.1	113
		201	202	203	204	205	206	207	208	209	210	211		209.5
If	IIf	153	151	150	148	145	140	131.5	124	115	117	121	82.3	112
		188	189	190	191	192	193	194	195	196	197	198		196
Ii	IIg	195	193	189	180	183	193	201	209	216	221	226	33.3	174
		226	228	230	232	234	236	238	240	242	244	246		232.5
IIa	IIj	226	224	220	216	207	202	203	204	204.5	205	205	45.4	201
						215	226	236	246	256.5	267	277		221
Ia	Il	210	207	202	196	188	192	201	207	210	212	213	43.5	182
			209	217	227	237	247	257	267	277	287	297		241
III	V	122	121	119	115	107	111	123	131	136	139	141	44.6	102
		136	140	145	149.5	155	160.5	166	171.5	177	183.5	190.5		157
IV	Ig	118	117	115	110.5	104	95	99	102	104.5	108	119	52.7	92
		192	190	188	185.5	183.5	181.5	179	177	175	173	171		181

[a] The melting points of the pure compounds are direct experimental values; the other temperatures were read from phase diagrams.

izability should increase with increasing molecular size. The first two factors should lead to a decrease in mesophase stability with increasing size of alkyl, the latter two to an increase. In the present case, however, the last two factors should be relatively unimportant since *n*-alkyl groups are flexible and only weakly polarizable; this explains why the nematic → liquid transition temperature decreases with increasing size of the alkyl group.

The stability of the mesophase should be greater, the greater the lateral adhesion of the rod-shaped molecules in question; this in turn should be greater, the greater the polarity and/or polarizability of the central parts of the rod-shaped molecule. In the *p*-phenylene *p*-alkoxybenzoates (I) there is mutual conjugation between the alkoxy and carboxy groups; this should increase the polarity of the carbonyl oxygen and so help to stabilize the mesophase. In the *p*-alkoxyphenyl terephthalates (II) such mutual conjugation is lacking; this could explain why, in each pair of isomers, I has the higher transition temperature.

We next extended our studies to analogous compounds I and II in which the terminal alkoxy groups were replaced by nitro-, chloro-, fluoro-, and ethoxycarbonyl. All these formed mesophases except the fluoro derivatives; here the virtual nematic → liquid transition temperatures were found by extrapolation[10] from phase diagrams for binary mixtures with the corresponding methoxy derivatives (Figures 3 and 4). In each case, the nematic → liquid transition lines were accurately linear; so the transition temperatures can be deduced with reasonable confidence. Table IV compares the transition temperature for compounds I and II with various terminal groups.

Table IV

Nematic → Liquid Transition Temperatures (°C)

	X =				
Compd	OMe	F	Cl	COOEt	NO_2
I	297	199	246	242	266
II	277	174	226	235	227

It will be seen that the isomers of series I again have higher transition temperatures than those of series II; this can also be rationalized in the terms indicated above. Thus mutual conjugation between an electron-releasing terminal group and the central carboxyl should stabilize the mesophase in the case of I but have little effect on II, whereas electron-withdrawing groups should have little effect on I but selectively destabilize the mesophase in II, for, in the latter case, mutual conjugation between the substituent and the oxygen atom *para* to it should make the latter positive and so reduce the resonance interactions between it and carbonyl. The net effect will be to make the carbonyl group less polar, and the arguments given above suggest that this

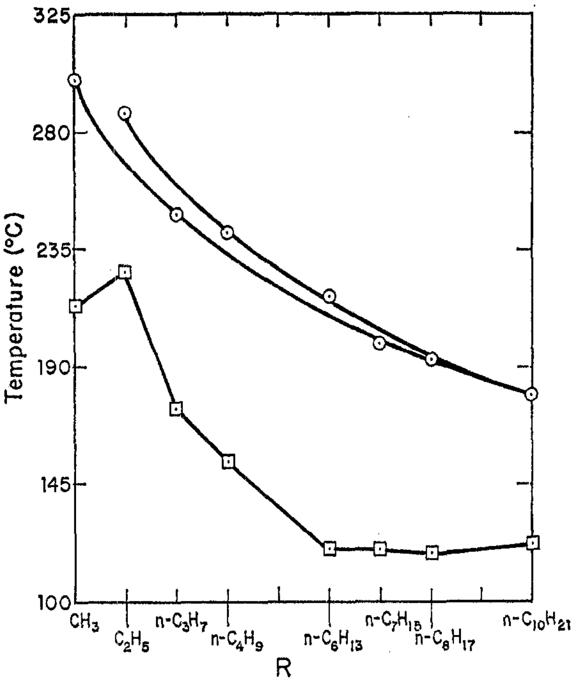

Figure 1.—Phase transition temperatures for the system of the *p*-phenylene esters of *p*-alkoxybenzoic acid.

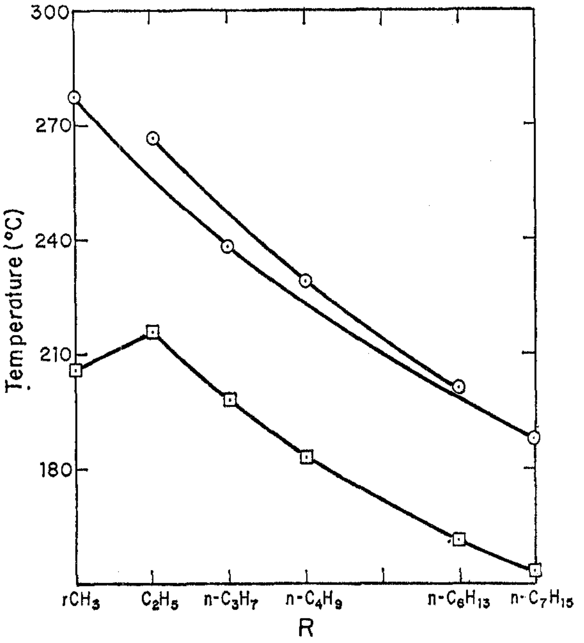

Figure 2.—Phase transition temperatures for the system of the *p*-alkoxyphenyl esters of terephthalic acid.

should lead to destabilization of the mesophase. Note that the difference in transition temperature between I and II is the same for the three $-E$ substituents (MeO, F, Cl), but much less for COOEt and much more for NO_2. Ethoxycarbonyl is a weakly $+E$ substituent which will probably have little effect on II; here the transition temperatures for I and II are quite similar. However, the very powerful $+E$ nitro group should have a very large effect on II; the difference in transition temperature is therefore about double the value for MeO, Cl, or F.

The relative effects of the groups can also be rationalized in similar terms. The mesophase stability would be expected to depend on the polarity of the terminal groups as well as that of the central ones; in the case of $-E$ substituents, the net polarity of the terminal group depends on two opposing factors, *i.e.*, the polarity of the σ bond (which makes the terminal group negative) and conjugation with the ring (which makes it positive). In the case of a strongly $-E$ group, one might expect the net charge on the terminal group to be positive owing to the mesomeric interaction. In this case the net charge should be less for fluorine or chlorine than methoxyl since fluorine and chlorine are more electronegative than oxygen and exert smaller $-E$ effects. The fact that chlorine lowers the transition temperature less than fluorine can also be rationalized on this basis, for chlorine has so little tendency to form π bonds that the net polarity of CCl (here $C^{\delta+} - Cl^{\delta-}$) may be greater than that of CF (where the σ and π polarities

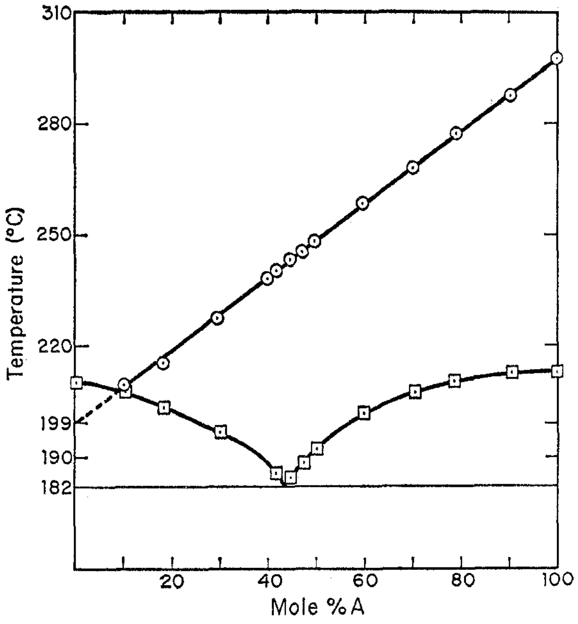

Figure 3.—The phase diagram for the system of *p*-phenylene-di-*p*-anisic ester (A) and *p*-phenylenedi-*p*-fluorobenzoic ester.

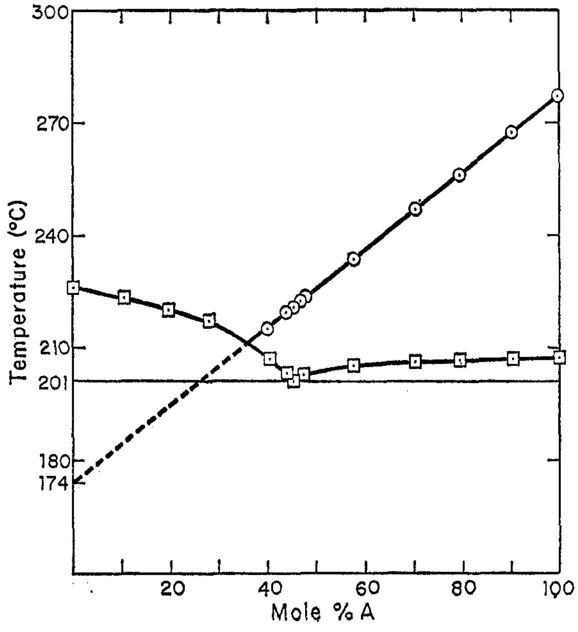

Figure 4.—The phase diagram for the system of di-*p*-methoxyphenyl terephthalate (A) and di-*p*-fluorophenyl terephthalate.

may almost cancel). The transition temperatures for X = Cl or F in I or II are therefore lower than for X = MeO. On the other hand ethoxycarbonyl is a bulky group with relatively low +E activity; such a group should tend to lower the transition temperature for geometrical reasons. The nitro group is a very polar group with strong +E activity; in the case of I, where +E activity is irrelevant, the polarity of nitro leads to a relatively large transition temperature. However, in the case of II, the +E activity of nitro leads to strong mutual conjugation with the *para* oxygen and so brings about a large decrease in the transition temperature.

These arguments suggest that the polarity of the groups concerned is the dominant factor; however, polarizability may also play a role. Thus, chlorine is more polarizable than fluorine; this could account for the fact that chlorine has the smaller destabilizing effect on the mesophase.

Mixed Liquid Crystals.—When an unsymmetrical molecule is dissolved in a nematic liquid crystal, it tends to orient itself in the unsymmetrical environment; for this reason liquid crystals offer interesting possibilities as solvents for spectroscopic studies, in particular by nmr.[3] In order to extend this technique to other fields of spectroscopy, it would be desirable to have a liquid crystalline medium that could be supercooled to a glass; it would also be advantageous to have as solvent some material which retained liquid crystallinity over a wide temperature range. One obvious way of achieving this is to use eutectic mixtures of materials forming liquid crystals, for, if the molecules in question are similar in shape, the nematic → liquid transition line is usually straight and the temperature range of the nematic form consequently greater for the eutectic mixture than for either component.

The isomers I and II obviously provide a very favorable example for this purpose and we have accordingly studied a number of binary systems of this type (Table III); a typical example is shown in Figure 5. Mixtures of this kind show relatively long mesophases and they have the further advantage over materials such as anils or azoxy compounds of being thermally and chemically stable. Such mixtures may prove of value in glpc for the separation of position isomers.[6]

We hoped that mixtures of our esters might be persuaded to form glasses since they supercool readily; thus the nematic → liquid transition of II (X = NO_2) could be observed quite easily in supercooled II, 15° below the melting point. Glasses of this kind could be very useful in spectroscopy (*cf.* ref 5); unfortunately, none of the systems studied could be converted to glasses even by very rapid quenching in liquid nitrogen.

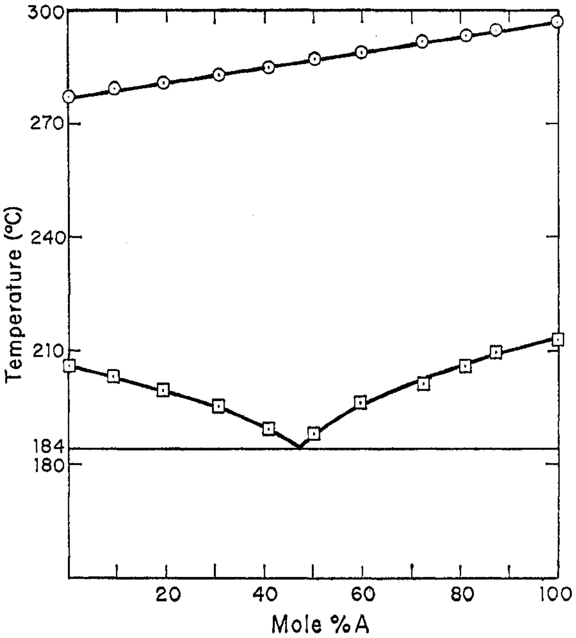

Figure 5.—The phase diagram for system of the *p*-phenylenedi-*p*-anisic ester (A) and di-*p*-methoxyphenyl terephthalate.

Registry No.—Ia, 1962-76-1; Ib, 24706-93-2; Ic, 24704-16-3; Id, 1818-98-0; Ie, 1818-99-1; If, 1819-00-7; Ig, 24706-96-5; Ih, 24704-18-5; Ii, 5411-00-7; Ij, 1819-02-9; Ik, 24706-98-7; Il, 24706-99-8; IIa, 24707-00-4; IIb, 24761-13-5; IIc, 24704-20-9; IId, 24707-01-5; IIe, 24707-02-6; IIf, 24728-02-7; IIg, 24707-03-7; IIh, 24707-04-8; IIi, 3838-05-9; IIj, 24707-06-0; III, 24707-07-1; IV, 24707-08-2; V, 24704-21-0.

Acknowledgment.—We are grateful to Dr. J. L. Ferguson for telling us his unpublished observations of smectic phases in If, Ig, and Ih.