

Molecular Structure and Liquid Crystallinity. Phenylene Bis(alkoxybenzoates)^{1a}SARDARI L. ARORA, JAMES L. FERGASON, AND TED R. TAYLOR^{1b}

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A number of 1,4-phenylene bis(4'-alkoxybenzoates) have been synthesized to study the effects of the central carboxyl groups on the formation of smectic phases and the thermal stability of the liquid crystal phases. A parallel series with methyl substituent at the 2 position of the 1,4-phenylene ring has also been prepared to investigate the effect of a lateral substituent on the mesomorphic properties. In addition to the nematic phase shown by these compounds, many of them also exhibit a smectic phase which is identical with smectic C. Many derivatives of the 2-methyl-1,4-phenylene series have lower melting points and higher nematic-isotropic transition temperatures than are commonly encountered in liquid crystalline compounds.

Our observation of a number of smectic phases in bis-(4'-*n*-alkoxybenzal)-1,4-phenylenediamines^{2a} led us to investigate what would happen to the formation of smectic phases if the central imine groups of these symmetrical molecules were replaced by carboxyl groups while the rest of the molecular structure remained the same.

The other aspect of this investigation was to study the influence of a lateral substituent; therefore 2-methyl-1,4-phenylene bis(4'-*n*-alkoxybenzoates) were also prepared. Further, these compounds, which are relatively inert, should be of interest as liquid crystalline solvents for many studies, *e.g.*, nmr,^{2b} esr,³ absorption spectroscopy,⁴ and gas chromatography.⁵

Experimental Section

Preparation of Materials. *p*-*n*-Alkoxybenzoic acids were prepared from *p*-hydroxybenzoic acid and the corresponding alkyl bromide according to the method of Gray and Jones.⁶

p-*n*-Alkoxybenzoyl chlorides were obtained by the usual method of refluxing the appropriate alkoxybenzoic acid (1 mol) with thionyl chloride (1.25 mol) in dry toluene in the presence of anhydrous pyridine (1 mol). After the refluxing and filtration of the pyridine hydrochloride, the solvent and the thionyl chloride were removed under reduced pressure from the filtrate and the residual acid chlorides were subsequently used for the preparation of the esters.

Hydroquinone and 2-Methylhydroquinone.—The commercial products were recrystallized before use.

1,4-Phenylene Bis(4'-*n*-alkoxybenzoates).—These were prepared by the dropwise addition of the hydroquinone (1 mol), dissolved in dry toluene and pyridine, to the solution of the corresponding alkoxybenzoyl chlorides (2 mol) in dry toluene. After the addition the reaction mixture was refluxed for 10–12 hr, filtered hot to remove the pyridine hydrochloride, and followed by the removal of the solvent under reduced pressure. The residual solid was cooled and triturated with ethanol to remove the unreacted starting materials, the product being less soluble in ethanol. After the filtration the solid was redissolved either in benzene or toluene and the solution dried over anhydrous sodium sulfate. The filtrate was concentrated under reduced pressure and the residual solution on cooling gave a solid material. The product in each case was recrystallized several times either

from chlorobenzene or hexane until the transition temperatures remained constant. These are listed in Table I. Three of

TABLE I
1,4-PHENYLENE BIS(4'-*n*-ALKOXYBENZOATES)^a

Compd	Substituents, R =	Transition temp, °C, from solid or preceding liquid crystal state to		
		Smectic	Nematic	Isotropic
1	C ₆ H ₁₃ O		124.4	212.9
2	C ₇ H ₁₅ O		121.6	199.0
3	C ₈ H ₁₇ O	121.9	125.6	194.9
4	C ₉ H ₁₉ O	128.4	135.7	186.4
5	C ₁₀ H ₂₁ O	126.7	146.6	181.7
6	C ₁₁ H ₂₃ O	111.0	151.1	175.0
7	C ₁₂ H ₂₅ O	109.1	155.7	171.5
8	C ₁₄ H ₂₉ O	105.4	157.3	162.5
9	C ₁₆ H ₃₃ O	108.1		156.4

^a Satisfactory combustion analytical data ($\pm 0.4\%$) were provided for compounds 1–9: Ed. ^b Transition from monotropic smectic.

these compounds, with the alkoxy chain lengths of C₆, C₇, and C₈, have been reported by Dewar, *et al.*,⁷ but the smectic phase of the latter two was not reported.

2-Methyl-1,4-phenylene bis(4'-*n*-alkoxybenzoates) were similarly prepared by refluxing the 2-methylhydroquinone (1 mol) with the appropriate alkoxybenzoyl chlorides (2 mol). Their subsequent purification and recrystallization were achieved by the same procedure as given for 1,4-phenylene bis(4'-alkoxybenzoates). The transition temperatures for these esters are listed in Table II.

TABLE II
2-METHYL-1,4-PHENYLENE BIS(4'-*n*-ALKOXYBENZOATES)^a

Compd	Substituents, R =	Transition temp, °C, from solid or preceding liquid crystal state to		
		Smectic	Nematic	Isotropic
1	C ₆ H ₁₃ O		87.8	171.8
2	C ₇ H ₁₅ O		84.5	159.6
3	C ₈ H ₁₇ O		72.4	156.0
4	C ₉ H ₁₉ O		76.6	148.5
5	C ₁₀ H ₂₁ O		79.5	144.3
6	C ₁₁ H ₂₃ O		81.6	138.0
7	C ₁₂ H ₂₅ O	80.2	87.8	136.1
8	C ₁₄ H ₂₉ O	81.0	101.5	126.5
9	C ₁₆ H ₃₃ O	86.1	110.2	122.7
10	C ₁₈ H ₃₇ O	91.0	112.7	117.9

^a Satisfactory combustion analytical data ($\pm 0.4\%$) were provided for compounds 1–10: Ed. ^b Transition from monotropic smectic.

Determination of Transition Temperatures.—The phase transition temperatures were determined both by differential thermal analysis (Du Pont DTA 900) and with a Leitz Panphot polarizing microscope using a Mettler FP-2 heating stage.

(7) M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965); M. J. S. Dewar and R. S. Goldberg, *J. Amer. Chem. Soc.*, **92**, 1582 (1970).

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(2) (a) S. L. Arora, T. R. Taylor, J. L. Ferguson, and A. Saupe, *J. Amer. Chem. Soc.*, **91**, 3671 (1969). (b) 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).

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

(4) G. P. Ceasar and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 191 (1969).

(5) H. Kelker, *Z. Anal. Chem.*, **198**, 254 (1963); M. J. S. Dewar and J. P. Schroeder, *J. Amer. Chem. Soc.*, **86**, 5235 (1964); *J. Org. Chem.*, **30**, 3485 (1965).

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

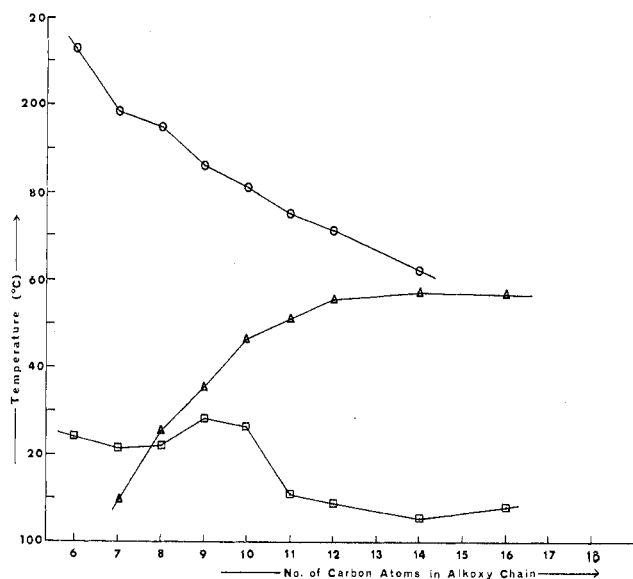


Figure 1.—Transition temperatures of 1,4-phenylene bis(4'-*n*-alkoxybenzoates) plotted against the number of carbon atoms in the alkyl chain of the ether group: ○, nematic-isotropic; △, smectic-nematic or isotropic; □, solid-liquid crystal.

Melting points (solid-isotropic liquid or solid-liquid crystal transitions), as determined by DTA thermograms, have been regarded as the transitions with the highest transition energy. Also, supercooling below the melting point occurs readily whereas it is negligible for isotropic-mesophase and mesophase-mesophase transitions.

Monotropic liquid crystal transition temperatures noticed below the melting points during the cooling operation of DTA thermograms were confirmed by reheating of the samples before crystallization. The assignments of the transition temperatures were confirmed by the polarizing microscope. The absolute error of the temperature measurements is estimated to be smaller than $\pm 2^\circ$. Plots of phase transition temperatures for the 1,4-phenylene bis(4'-alkoxybenzoates) are shown in Figure 1 and in Figure 2 for the 2-methyl substituted homologs.

Results and Discussion

We shall first examine the liquid crystal properties of the corresponding compounds of the two phenylene alkoxybenzoate series as represented by Figure 3 (a and b). Trans rather than cis configurations have been used because the former result in a more linear, rodlike molecular shape, a general requisite for the mesophase to occur.⁸ A survey of similar liquid crystal transition temperatures, that is nematic-isotropic, smectic-nematic, or smectic-isotropic (Tables I and II) for any two corresponding homologs shows that such temperatures are much lower in the 2-methyl-1,4-phenylene bis(4'-*n*-alkoxybenzoates). These decreases in the thermal stabilities of liquid crystal phases, according to Gray,⁹ may be attributed to the broadening effect caused by a lateral substituent in an otherwise relatively linear molecule. An increase in the breadth forces the long axes of the molecules apart, as a result of which the interactions are decreased and consequently the liquid crystal transition temperatures are lowered. This is in part true, but the effect of a lateral substituent on the molecular geometry cannot be ignored, as the geometry contributes significantly to the double bond

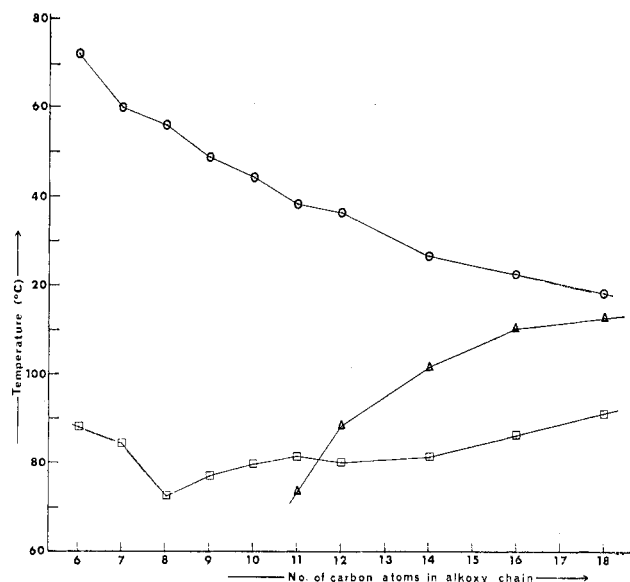


Figure 2.—Transition temperatures of 2-methyl-1,4-phenylene bis(4'-*n*-alkoxybenzoates) plotted against the number of carbon atoms in the alkyl chain of the ether group: ○, nematic-isotropic; △, smectic-nematic or isotropic; □, solid-liquid crystal.

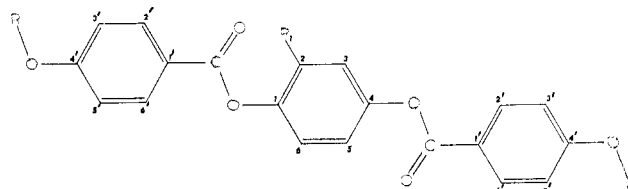


Figure 3.—Trans configuration of 1,4-phenylene bis(alkoxybenzoates): R = alkyl chain; (a) $R_1 = H$; (b) $R_1 = CH_3$.

character of otherwise normal single bonds especially when the system involved is a conjugated one.

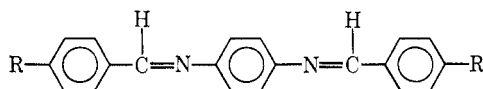
In the molecular configuration of the unsubstituted 1,4-phenylene bis(4'-alkoxybenzoates), as represented by the structural formula (Figure 3a), maximum overlap of the p orbitals and subsequent mutual conjugation, between the alkoxy and the carbonyl, the carbonyl and the oxygen, and the central aromatic ring with the oxygens, will take place if all the parts of the molecule are coplanar. Any factor or factors which oppose such a configuration, depending on the twists around the single bonds of the conjugated system, will reduce the overlap of the p orbitals and in turn the degree of conjugation.

A change in the degree of conjugation will alter both the polarizability and the resultant moments of the molecule, the latter due to an effect on the mesomeric moments. The effect of the change in the resultant moments is difficult to estimate; however, a decrease in the polarizability will decrease the dispersive forces. Consequently, the decrease in polarizability will cause a decrease in the thermal stabilities of the liquid crystal phases.

A coplanar configuration for 1,4-phenylene bis(4'-alkoxybenzoates) does not appear to be feasible because in such a molecular geometry the oxygen atoms of the carbonyl groups will be bumping into the nonbonded sides of the adjacent hydrogens at positions 2 or 6 and 3 or 5 of the central aromatic ring thereby causing a considerable strain on the molecule. In order to avoid this situation, some twist around the C_1-O and C_4-O

(8) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962, p 149.

(9) G. W. Gray, *Mol. Cryst.*, **1**, 333 (1966).

TABLE III
 BIS(4'-*n*-ALKOXYBENZAL)-1,4-PHENYLENEDIAMINES


Compd	Substituents, R =	Transition temp, °C, from solid or preceding liquid crystal state to						
		Smectic 5	Smectic 4	Smectic 3	Smectic 2	Smectic 1	Nematic	Isotropic
1	C ₆ H ₁₃ O		155	160	167	168	187	255
2	C ₇ H ₁₅ O	125	148	155	161	168	198	240
3	C ₈ H ₁₇ O	119	143	150	154	164	203	232
4	C ₉ H ₁₉ O	120	145	148	149	163	206	223
5	C ₁₀ H ₂₁ O	123	140	144	145	163	208	218
6	C ₁₂ H ₂₅ O		122	131	134	157	204	205
7	C ₁₄ H ₂₉ O		123	126	127	153		197
8	C ₁₆ H ₃₃ O				128	149		189
9	C ₁₈ H ₃₇ O				129	147		183

bonds will occur. This twist, however small it may be, will force both the end aromatic rings together with the ester linkages out of the plane of the central aromatic ring, thus reducing the coplanarity of the molecule.

Rotation around the CO-O bonds does not appear to be reasonable, because this will not only bring the hydrogens of the central ring in contact with the carbon of the carbonyls but will also destroy the linearity of the molecule.

Since the end groups are free to rotate in either direction with reference to the central aromatic ring, the twists about C₁-O and C₄-O in the phenylene alkoxybenzoates would be identical. Therefore, the twisting here would be symmetrical.

In the 2-methyl-1,4-phenylene bis(4'-alkoxybenzoates) the situation is different. When a substituent is on the central ring, its position being ortho to the ester linkage, the twisting around the C₁-O bond is going to be different due to the steric factor of the methyl as compared to the twist around the C₄-O bond. This may result in unsymmetrical twisting in these molecules and thus further reduce the coplanarity of the molecules. This in turn will decrease the polarizability of the laterally substituted compounds when compared to the unsubstituted ones; there will also be a change in the resultant moments. Thus we would expect a decrease in the thermal stabilities of the liquid crystal phases in the laterally substituted derivatives. These decreases will, however, be further enhanced due to the breadth increasing effect of a lateral substituent on the molecule.

Even the melting points of the laterally substituted derivatives are much lower when compared with those of the corresponding homologs of the nonlaterally substituted series. These differences may be partially due to the steric factor present in the laterally substituted compounds causing a reduction in the resultant moments of the molecules and consequently the intermolecular interactions are relatively weakened.

Figures 1 and 2 are the plots of the transition temperatures against the number of carbons in the alkyl chain. All the homologs in case of 1,4-phenylene bis(4'-alkoxybenzoates) with a chain length of C₅ to C₁₂ and C₁₄ show a nematic phase. In addition to the nematic phase homologs of this series, C₈ to C₁₂ and C₁₄ exhibit a smectic phase. Only a smectic phase is observed when the alkyl chain is C₁₆. In the case of the C₇ homolog a monotropic smectic phase is also observed. However, in the case of 2-methyl-1,4-phenylene bis(4'-alkoxybenzoates) all the homologs show a nematic phase. In ad-

dition, when the chain length is C₁₂, C₁₄, C₁₆, and C₁₈, a smectic phase is also observed. A monotropic smectic phase is noted in case of the C₁₁ homolog.

Because of the regular behavior of the transition temperatures, significant details can be observed as a difference of the similar liquid crystal transition temperatures for the corresponding homologs. These temperature differences, though small, are real since errors in relative temperatures are certainly not $> \pm 0.2^\circ$; they, when plotted for the nematic transitions, result in two curves (Figure 4), one for the odd number alkyl chain lengths and the other for the even ones. Since the geometrical configuration of the chain in both the cases can be assumed to be nearly the same, the odd and even alternation of the differences in the clearing points, which converge and nearly vanish at the C₉ homologs, may be attributed to the differences in the polarizability and the small configurational changes caused by the lateral methyl on the neighboring molecules.

When we compare the temperature differences for smectic transitions (Figure 4), a quite different behavior is observed. That is, the temperature difference behaves nearly exponentially with chain length. This may indicate that the long hydrocarbon chain plays an increasingly significant role in the formation of the smectic phase by direct interactions.

The influence of central carboxyl groups, when substituted for the imine linkages in analogous compounds, may be seen by comparing similar liquid crystal transition temperatures of the homologs of 1,4-phenylene bis(4'-*n*-alkoxybenzoates) and bis(4'-*n*-alkoxybenzal)-1,4-phenylenediamines (Table I and III). Transition temperatures are lower in case of phenylene alkoxybenzoates, which indicate a reduction of intermolecular interactions. It has been mentioned earlier that the thermal stabilities of these phases are affected both by the breadth and the molecular geometry of the molecule.

Let us first consider the breadth of these molecules. In Figure 5 the two structures are compared on the basis of their planar configurations. This comparison would indicate that the breadths of the two molecules are approximately the same and therefore their effect in reducing the thermal stabilities of the liquid crystal phases is not significant. A further factor in determining their thermal stabilities is the molecular geometry. We have previously shown that molecules of phenylene alkoxybenzoates are likely to have a nonplanar configuration. If we examine the molecular structure of the bis(alkoxybenzal)phenylenediamines, we observe

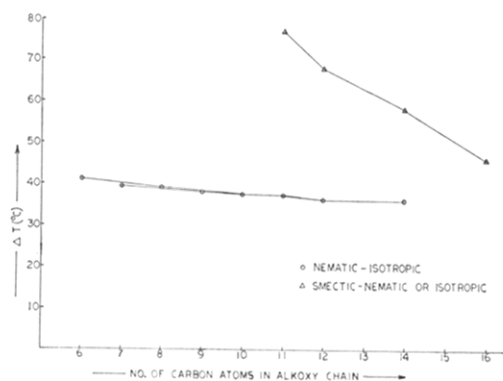


Figure 4.—Temperature differences between similar mesophase transition temperatures of the corresponding compounds of the two phenylene benzoate series plotted against the number of carbon atoms in the alkyl chain of the ether group.

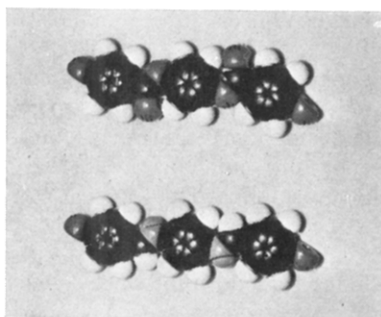


Figure 5.—Planar structures represented by CPK models: phenylene benzoates (top) and phenylenediamines (bottom). The terminal oxygens are without the alkyl chains.

that for a planar geometry the nonbonded side of the hydrogen of the C-H bond of the imine linkages is extremely close and is probably touching the nonbonded side of one of the hydrogens of the central aromatic ring which are ortho to the imine linkages. These steric and repulsive interactions would tend to cause a twist around the single bonds of C₁-N and C₄-N. Due to the twists around these bonds, their π -bonding character would be decreased, and, therefore, the mutual conjugation along the entire molecule would be decreased.

Twisting around single bonds in similar type of compounds has been recently determined in the nonplanar structure of terephthalbis(4-fluoroaniline),¹⁰ where the twist angle around the C-N bond is found to be about 30°. Similar nonplanar configurations for aromatic azomethines¹¹ have been suggested.

Since the hydrogen atom is much smaller than the oxygen atom, it would be reasonable to assume that the twists in the case of the diamines would be much smaller than the corresponding twists in the benzoates. Thus, the diamines would be more planar than the comparable benzoates. In other words, the phenylenediamine will have a more anisotropic polarizability because of a higher degree of conjugation along the long axis of the molecule when compared with the corresponding phenylene benzoate. Due to the higher anisotropy in phenylenediamine molecules the thermal stabilities of their liquid crystal phases are higher when compared with those of the corresponding phenylene benzoates.

This leads to the conclusion that the molecular geom-

(10) N. Bravo, J. W. Doane, S. L. Arora, and J. L. Ferguson, *J. Chem. Phys.*, **50**, 1398 (1969).

(11) V. I. Minkin, Y. A. Zhdanov, E. A. Medyantzeva, and Y. A. Ostroumov, *Tetrahedron*, **23**, 3651 (1967).

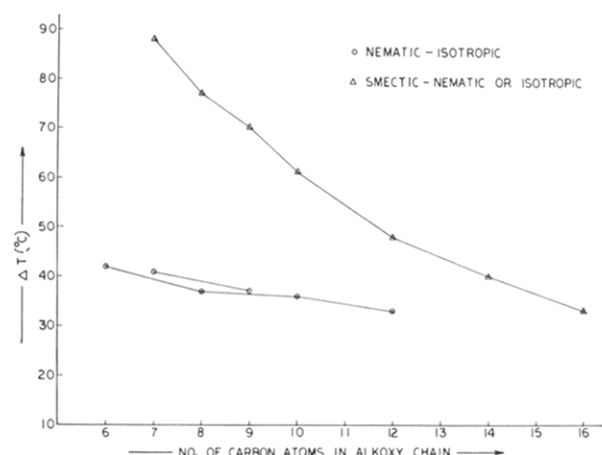


Figure 6.—Temperature differences between similar mesophase transition temperatures of the corresponding compounds of 1,4-phenylene bis(4'-*n*-alkoxybenzoates) and bis(4'-*n*-alkoxybenzal)-1,4-phenylenediamines plotted against the number of carbon atoms in the alkyl chain of the ether group.

etry is very important and plays a significant role in establishing the thermal stabilities of the liquid crystal phases.

In addition to increasing the thermal stabilities of the liquid crystal phases, replacement of central carboxyl groups by imine linkages in the analogous compounds increases the number of smectic phases. Temperature differences for similar liquid crystal transitions in case of the corresponding compounds of these two series are plotted against the number of carbons in the terminal chain length in Figure 6. A plot very similar to Figure 4 is obtained, with the same trend to decreasing temperature difference with increasing alkoxy chain length. The reason smectic 2 or any other lower temperature smectic phase is not observed in the case of the phenylene benzoates is that the same trend of decreasing transition temperatures may continue as is observed in the case when the smectic-nematic transitions for two corresponding homologs are compared. Thus, the other smectic phases may possibly be monotropic below the melting points of the phenylene benzoates. Unfortunately, the phenylene benzoates do not supercool readily and crystallization takes place near the melting point. At the present this is the only explanation we have for reduction in the number of smectic phases.

The smectic phase observed for both the laterally and nonlaterally substituted phenylene benzoates as well as smectic 1 of the phenylenediamines is identical with the smectic C of Sackmann and Demus.¹² Optical studies show that the smectic C phase observed is biaxial in character and is similar to the smectic C phase reported in our earlier publication.¹³

Registry No.—Table I—1, 1818-99-1; 2, 1819-00-7; 3, 24706-96-5; 4, 26314-50-1; 5, 24704-18-5; 6, 26314-52-3; 7, 26358-45-2; 8, 26314-53-4; 9, 26358-46-3; Table II—1, 26314-54-5; 2, 26314-55-6; 3, 26314-56-7; 4, 26314-57-8; 5, 26314-58-9; 6, 26314-59-0; 7, 26314-60-3; 8, 26314-61-4; 9, 26314-62-5; 10, 26358-47-4; Table III—1, 24679-00-3; 2, 24679-01-4; 3, 24679-02-5; 4, 25783-12-4; 5, 24679-03-6; 6, 25955-15-1; 7, 25955-16-2; 8, 24679-04-7; 9, 24679-05-8.

(12) H. Sackmann and D. Demus, *Mol. Cryst.*, **2**, 81 (1966).

(13) T. R. Taylor, J. L. Ferguson, and S. L. Arora, *Phys. Rev. Lett.*, **24**, 359 (1970).