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Synthesis and Mesomorphic Properties of Phenyl 4-Benzoyloxybenzoate Derivatives†

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Abstract—A series of liquid crystalline materials comprising substituted phenyl 4-benzoyloxybenzoates were prepared. These compounds may be viewed as derivatives of the unsymmetrical molecule, *p*-hydroxybenzoic acid. The mesomorphic properties of these new compounds were compared with the more symmetrical analogs derived from hydroquinone or terephthalic acid which have been reported in the literature. The crystal-to-mesophase transition temperatures for the unsymmetrical materials were significantly lower than those of the corresponding symmetrical derivatives, whereas the mesophase-to-isotropic transition temperature varied only slightly for R = R′. The stability of the mesophase (N→I transition) for the unsymmetrical materials fell between those of the corresponding hydroquinone and terephthalic acid derivatives, as anticipated from electronic considerations. The resulting decrease in the crystal-to-mesophase transition temperature was accompanied by an increase in the mesomorphic range. For example, the nematic range of 4-chlorophenyl 4-(chlorobenzoyloxy)benzoate is 141–237 °C, ($\Delta T = 96°$), compared with 226–246 °C, ($\Delta T = 20°$), for *p*-phenylene bis(*p*-chlorobenzoate) and 195–226 °C, ($\Delta T = 31°$), for bis(*p*-chlorophenyl) terephthalate. The effects of lateral and terminal substituents on the mesomorphic properties of these unsymmetrical compounds and their additive nature are discussed.

1. Introduction

In view of the recent upsurge of interest in room temperature nematic materials and in particular in their use in various electro-optical applications,[1,2] we are continuing our work towards preparing liquid crystals with low crystal-to-nematic (C–N) transition temperatures. The ester group was selected as the central linkage, since it should offer stability advantages over the more commonly

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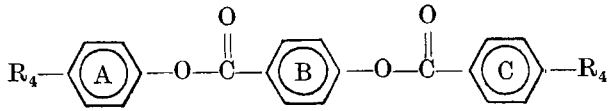
used Schiff base materials. The first paper[3] in this series dealt with liquid crystals comprising alkyl- and alkoxy-substituted phenyl benzoates. These compounds had relatively narrow mesomorphic ranges; none was nematic at room temperature. A room temperature nematic mixture was obtained, however, by suitable mixing. The present paper deals with liquid crystals derived from phenyl 4-benzoyloxybenzoate (I). This system was selected for a number of reasons. First, it was known from the work of Dewar[4] and others[5]



I

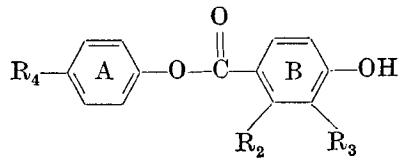
that liquid crystals derived from hydroquinone or terephthalic acid, although having crystal-to-mesophase (C–M) transition temperatures above 100 °C, have relatively broad mesomorphic ranges. Second, the increased dissymmetry associated with liquid crystals of structure I should result in less efficient packing in the crystal lattice and hence lead to lower crystal-to-mesophase transition temperatures. Also, because of the relatively high thermal stability of the mesophase for liquid crystals containing three *p*-phenylene groups, compounds in this class should be able to accommodate one or more lateral substituents. The lateral substituent would also be expected to contribute to the dissymmetry of the liquid crystal molecule with the possibility of an additional lowering of the crystal-to-mesophase transition. The position and polarity of the lateral substituent will also influence other physical properties of the molecules (dielectric and conductivity anisotropies) which would therefore give more flexibility in device applications, since the room temperature nematic range requirement is only one of many physical properties which must be controlled.

2. Experimental

The substituted phenyl 4-benzoyloxybenzoates were prepared by the reaction of the substituted benzoyl chloride with the substituted phenyl 4-hydroxybenzoates in pyridine solution at room temperature. The products were purified by recrystallization from suitable solvents

or by column chromatography. The substituted phenyl 4-hydroxybenzoates (Table 1) were prepared by the acid-catalyzed esterification of phenols following the procedure of Lowrance.[6] An example of this procedure is given below for 4-ethoxyphenyl 4-hydroxybenzoate. The transition temperatures were determined in open capillary tubes with an A. H. Thomas melting point apparatus. The liquid

TABLE 1 Substituted Phenyl 4-Hydroxybenzoates[a]



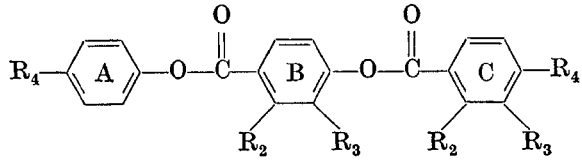
Ring Substituent			
A	*B*		
R_4	R_2	R_3	mp (°C)
OCH_3	H	H	191–193
OC_2H_5	H	H	204–207
OC_5H_{11}	H	H	154–156
OC_5H_{11}	H	Cl	157–159
OC_8H_{17}	H	H	151–153
OC_8H_{17}	H	Cl	143–144
C_3H_7	H	H	148–150
C_5H_{11}	H	H	145–147
C_5H_{11}	H	Cl	137–139
C_5H_{11}	Cl	H	149–151
C_8H_{17}	H	H	126–128
C_8H_{17}	H	Cl	124–126
C_8H_{17}	Cl	H	133–135
Cl	H	H	194–196

[a] All alkyl and alkoxy groups are normal.

crystals prepared in this work are recorded in Table 2 along with their mesomorphic transition temperatures. Satisfactory elemental analyses were obtained for all compounds.

4-Ethoxyphenyl 4-Hydroxybenzoate To a suspension of *p*-ethoxyphenol (20.7 g, 0.15 mol) and *p*-hydroxybenzoic acid (13.8 g, 0.10 mol) in toluene (500 ml) were added concentrated sulfuric acid (0.5 g) and boric acid (0.31 g) (5 mol %). The reaction mixture was heated under reflux for 21 h under a Dean–Stark trap. The solvent was then

TABLE 2 Substituted Phenyl 4-Benzoyloxybenzoate Liquid Crystals[a]



Compound Number	Ring Substituent A	B		C			Transition Temperatures (°C)[b]	ΔT°c
	R_4	R_2	R_3	R_2	R_3	R_4		
1	OCH_3	H	H	H	H	OCH_3	145–284	139
2	OCH_3	H	H	H	H	OC_5H_{11}	154–238	84
3	OCH_3	H	H	Cl	H	Cl	132–204	72
4	OC_2H_5	H	H	H	H	H	153–167	14
5	OC_2H_5	H	H	H	H	OCH_3	144–284	140
6	OC_2H_5	H	H	H	H	OC_2H_5	132–279.5	147.5
7	OC_2H_5	H	H	H	H	OC_5H_{11}	129–239.5	110.5
8	OC_2H_5	H	H	H	H	CH_3	150–257	107
9	OC_2H_5	H	H	H	H	F	140–231	91
10	OC_2H_5	H	H	H	H	Cl	149–258.5	109.5
11	OC_2H_5	H	H	H	OCH_3	H	118–121[d]	—
12	OC_2H_5	H	H	OCH_3	H	OCH_3	144–171	27
13	OC_2H_5	H	H	H	F	H	146–153	7
14	OC_2H_5	H	H	Cl	H	H	124–127 (121)	—
15	OC_2H_5	H	H	Cl	H	Cl	119–205	86
16	OC_2H_5	H	H	H	Cl	H	151–154 (120)	—
17	OC_2H_5	H	H	H	Cl	Cl	145–189	44
18	OC_5H_{11}	H	H	H	H	OCH_3	123–239	116
19	OC_5H_{11}	H	H	H	H	OC_5H_{11}	108–214	106
20	OC_5H_{11}	H	H	Cl	H	Cl	80–173	93
21	OC_5H_{11}	H	Cl	Cl	H	Cl	71.5–116	44.5
22	OC_8H_{17}	H	H	H	H	OCH_3	104–218	114
23	OC_8H_{17}	H	H	H	H	OC_8H_{17}	84§162.5–189	26.5
24	OC_8H_{17}	H	H	H	H	CH_3	113–193	80
25	OC_8H_{17}	H	H	H	H	C_5H_{11}	87–182	95
26	OC_8H_{17}	H	Cl	H	H	OCH_3	91–169.5	78.5
27	OC_8H_{17}	H	Cl	H	H	OC_8H_{17}	75§81–148	67
28	OC_8H_{17}	H	Cl	H	H	C_5H_{11}	70–138	68
29	OC_8H_{17}	H	H	Cl	H	Cl	83–163	80
30	OC_8H_{17}	H	Cl	Cl	H	Cl	75–109	34
31	Cl	H	H	H	H	Cl	141–237	96
32	Cl	H	H	Cl	H	Cl	141–176.5	35.5
33	C_3H_7	H	H	H	H	OCH_3	110–243.5	133.5
34	C_3H_7	H	H	H	H	OC_5H_{11}	115–209	94
35	C_5H_{11}	H	H	H	H	H	108–120	12
36	C_5H_{11}	H	H	H	H	CH_3	105–199.5	94.5
37	C_5H_{11}	H	H	H	H	C_3H_7	78–188	110
38	C_5H_{11}	H	H	H	H	C_5H_{11}	78–179.5	101.5
39	C_5H_{11}	H	H	H	H	C_7H_{15}	76§103.5–168.5	65
40	C_5H_{11}	H	H	H	H	OCH_3	87–223	136

Compound Number	Ring Substituent A	B		C			Transition Temperatures (°C)[b]	ΔT°c
	R_4	R_2	R_3	R_2	R_3	R_4		
41	C_5H_{11}	H	H	H	H	OC_4H_9	89–209.5	120.5
42	C_5H_{11}	H	H	H	H	$OCH_2CH(CH_3)_2$	110–179.5	69.5
43	C_5H_{11}	H	H	H	H	OC_5H_{11}	91–198.5	107.5
44	C_5H_{11}	H	H	H	H	SC_5H_{11}	117–168.5	51.5
45	C_5H_{11}	H	H	H	H	F	102–180.5	78.5
46	C_5H_{11}	H	H	H	H	Cl	113S139–212	73
47	C_5H_{11}	H	H	H	H	Br	123S149–213	64
48	C_5H_{11}	H	H	H	H	CN	125S139–249	110
49	C_5H_{11}	Cl	H	H	H	C_5H_{11}	39–122	83
50	C_5H_{11}	H	Cl	H	H	C_5H_{11}	67–130	63
51	C_5H_{11}	H	Cl	H	H	C_7H_{15}	55–119	64
52	C_5H_{11}	H	H	Cl	H	OCH_3	109–168.5	59.5
53	C_5H_{11}	H	Cl	H	H	OC_5H_{11}	70–151	81
54	C_5H_{11}	H	Cl	H	H	$OC_{12}H_{25}$	73.5–126	52.5
55	C_5H_{11}	H	Cl	H	H	$OCH_2CH(CH_3)_2$	94–126	32
56	C_5H_{11}	H	Cl	H	Cl	OC_5H_{11}	83–123	40
57	C_5H_{11}	H	H	H	Cl	OC_5H_{11}	119–168	49
58	C_5H_{11}	H	H	H	F	H	108–117	9
59	C_5H_{11}	Cl	H	H	H	Cl	91–150	59
60	C_5H_{11}	H	Cl	H	H	Cl	112–155	43
61	C_5H_{11}	H	H	Cl	H	Cl	87–153.5	66.5
62	C_5H_{11}	H	H	H	Cl	Cl	111S129–149.5	20.5
63	C_5H_{11}	H	Cl	Cl	H	Cl	82–89	7
64	C_5H_{11}	H	Cl	H	Cl	Cl	109–112 (93)	—
65	C_8H_{17}	H	H	H	H	CH_3	107–173	66
66	C_8H_{17}	H	H	H	H	OCH_3	90–195	105
67	C_8H_{17}	Cl	H	H	H	CH_3	78–117.5	39.5
68	C_8H_{17}	H	Cl	H	H	C_7H_{15}	70–106	36
69	C_8H_{17}	Cl	H	H	H	C_7H_{15}	39–104.5	65.5
70	C_8H_{17}	Cl	H	H	H	$C_{12}H_{25}$	57S88–98	10.0
71	C_8H_{17}	Cl	H	H	H	$OC_{12}H_{25}$	85S114–121	7

[a] All alkyl and alkoxy groups are normal unless otherwise indicated.
[b] S indicates the occurrence of a smectic phase.
[c] Range of nematic mesophase.
[d] No mesophase detected.
( ) Monotropic transition.

removed under reduced pressure, and the product was washed with ethyl ether/513 ligroin (1:1). The resulting 4-ethoxyphenyl 4-hydroxybenzoate (23.1 g, 90%, mp 200–206 °C) was recrystallized from acetonitrile to give 18.5 g, 72% of pure product, mp 204–207 °C.

3. Results and Discussion

The substituted phenyl 4-benzoyloxybenzoate liquid crystals prepared in this work can be considered as derivatives of 4-hydroxybenzoic acid. Because of the increased dissymmetry associated with liquid crystals of this type compared with the corresponding liquid crystals from hydroquinone or terephthalic acid, one might expect less efficient packing in the crystal lattice and hence lower crystal-to-mesophase transition temperatures for these molecules. Table 3 shows a comparison of the phenyl 4-benzoyloxybenzoates with symmetrical end groups and the related hydroquinone or terephthalic acid derivatives, some of which have been previously described in the literature. In addition, the results in Table 3 show a substantial reduction in the C–M transition temperature for the phenyl 4-benzoyloxybenzoates, compared with the more symmetrical analogs. We assume that this is a result of the less efficient packing in the crystal lattice for the unsymmetrical compounds. The decrease

TABLE 3 Comparison of Central Linkage Symmetry

p-Substituent[a]	*p*-Phenylene Dibenzoate		Diphenyl Terephthalate		Phenyl 4-Benzoyloxybenzoate	
	Nematic Range (°C)	$\Delta T°$	Nematic Range (°C)	$\Delta T°$	Nematic Range (°C)	$\Delta T°$
OCH_3	213–297[b]	84	205–277[b]	72	145–284	139
OC_2H_5	226–287[b]	61	216–266.5[b]	50.5	132–279.5	147.5
OC_5H_{11}	145–222[c]	77	167–213[d]	46	108–214	106
C_5H_{11}	123–185.5[e]	62.5	152–178[e]	26	78–179.5	101.5
Cl	226–246[b]	20	195–226[b]	31	141–237	96

[a] All alkyl and alkoxy groups are normal.

[b] Dewar, M. J. S. and Goldberg, R. S., *J. Org. Chem.* **35**, 2711 (1970).

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

[d] Kelker, H. and Scheurle, B., *J. Physique* **30-C4**, 104 (1969).

[e] Prepared for this study.

ranges from 37 to 84 °C compared with the lowest-melting symmetrical isomer. Since the overall length and molecular geometry are quite similar for each set of the three isomeric compounds, one would expect that the thermal stability of the respective mesophases would also be similar. The experimental results verify this. Therefore, the nematic range of the phenyl 4-benzoyloxybenzoate liquid crystals has been extended significantly as a result of the lower C–M transition temperatures.

Dewar[4] has explained the higher nematic-to-isotropic transition temperatures of the *p*-phenylene bis(4-alkoxybenzoate) esters compared with the isomeric terephthalate esters in terms of increased polarizability of the central linkages of the phenylene ester as a result of the mutual conjugation between the alkoxy and carboxy group. The alkyl group would be expected to act similarly. The electron withdrawing effect of the chloro substituent destabilizes the mesophase of the bis(4-chlorophenyl) terephthalate relative to the hydroquinone isomer by making the carbonyl group less polarizable as a result of the increased positive character of the oxygen atom; this will decrease the resonance interaction between the oxygen atom and the carbonyl group. The electronic interactions of the phenyl 4-benzoyloxybenzoate liquid crystals would be expected to stabilize the nematic mesophase to an intermediate extent. It is rather remarkable, therefore, that the nematic-to-isotropic (N–I) transition temperatures for the liquid crystals recorded in Table 3 fall between those of the symmetrical isomers. The unique structural nature of the nematic mesophase results in a normalization of the various crystal arrangements to a state of relatively similar molecular arrangement. This arrangement allows the more subtle molecular effects, both steric and electronic, to be reflected in something as simple as a nematic-to-isotropic transition temperature.

In addition to the dissymmetry of the phenyl 4-benzoyloxybenzoate system itself, we have also considered nonequivalent terminal substituents in order to introduce more dissymmetry into the individual molecules. A recent paper by Haut[7] has explored the use of this concept in an attempt to prepare unsymmetrical *p*-phenyl ene bis(4-alkoxybenzoates) with low crystal-to-mesophase transition temperatures. However, the C–M temperatures for these compounds were at most only 15 °C below those of the symmetrically substituted

materials. It was of interest to compare the phenyl 4-benzoyloxybenzoates with the *p*-phenylene esters, both with unsymmetrical terminal substitution, in order to assess the effect of the additive nature, if any, of the central linkage and terminal substituents on lowering the crystal-to-mesophase transition temperatures. Compounds 2 and 18 from Table 2, with pentyloxy and methoxy substitution, have C–N transition temperatures of 154° and 123°C respectively. The methoxy-pentyloxybenzoate ester taken from Haut's work has a C–N transition temperature of 137 °C. Thus, the dissymmetry introduced by the central linkage for our materials does not always result in the lowest crystal-to-mesophase transition temperature. One of the isomeric phenyl 4-benzoyloxybenzoates (Compound 18) does have a C–N transition temperature 14 °C lower than the corresponding symmetrical central linkage material.† While we have obtained a lowering of the C–N transition temperature, the decrease is relatively small and may reflect a gradual levelling-off of the C–N transition temperatures to a point where dramatic decreases are not likely to occur for variations in terminal alkoxy substitution only. This is in keeping with Haut's work in that as the carbon chain is lengthened, the crystal-to-mesophase transition temperatures of the unsymmetrical phenylene esters converge to a point which is only slightly below that of the symmetrical derivatives with long alkoxy substituents.

At this point, we would like also to comment on the relative thermal stability of the nematic mesophase for these three isomeric compounds. The electronic properties of the methoxy and pentyloxy groups are assumed to be similar, and therefore, the interchange of these groups, as in compounds 2 and 18, would not change the polarizability of the central linkage. This should be reflected in a similar mesomorphic thermal stability for these two compounds, i.e. the N–I transition temperatures should be nearly the same. The observed N–I transition temperatures for these compounds (238 ° and 239 °C) support this reasoning. In addition, the corresponding hydroquinone derivative would be expected to have the most thermally stable mesophase, since the direct interaction of the alkoxy groups with the carbonyl of the ester group can occur from both ends

† A rigorous comparison of these materials would require the preparation of the 4-methoxyphenyl-4-pentyloxyphenyl terephthalate ester.

of the molecule, whereas in the phenyl 4-benzoyloxybenzoates, this interaction is blocked by an oxygen atom in half of the molecule. The increased polarizability of the central linkages of the hydroquinone derivative would tend to stabilize the mesophase, as indicated by the higher nematic–topisotropic transition temperature of 253 °C.

We have previously mentioned[3] that the replacement of an oxygen atom adjacent to the phenyl ring with a methylene group resulted in the destabilization of all phases. A similar effect was noted for the substituted phenyl 4-benzoyloxybenzoates, as recorded in Table 4.

TABLE 4 Alkyl versus Alkoxy Groups of Equivalent Chain Length[a]

Ring Substituent					
A	*C*	Nematic	Compound	Decrease in	Decrease in
R_4	R_4	Range (°C)	Number	C–N (°C)	N–I (°C)
OC_2H_5	OCH_3	144–284	5		
C_3H_7	OCH_3	110–243.5	33	34	40.5
OC_2H_5	OC_5H_{11}	129–239.5	7		
C_3H_7	OC_5H_{11}	115–209	34	14	30.5
C_5H_{11}	OC_4H_9	89–209.5	41		
C_5H_{11}	C_5H_{11}	78–179.5	38	11	30.5

[a] All alkyl and alkoxy groups are normal.

The substitution of an alkyl group for an alkoxy group with the same number of atoms resulted in decreases in the crystal-to-nematic transition temperature of 11° to 34 °C. The larger decreases are associated with liquid crystals having relatively short chain lengths, and as the terminal substituents are lengthened, the decrease in the C–N transition temperature becomes smaller for a given alkyl–alkoxy substitution. This is another example of the limiting effect for structural variations in homologous series of liquid crystals, i.e., for a given structural change, the most pronounced changes in phase transition temperatures are associated with the lower homologs. As the length of the terminal substituent increases, these changes tend to diminish.

The clearing point of the phenyl 4-benzoyloxybenzoates was

found to decrease with an increase in carbon chain length; compare compounds 36–39 in Table 2.

Liquid crystals containing three *p*-phenylene groups with ester[4] or imine[8] central linkages are known to have broad mesomorphic ranges of high thermal stability. The introduction of a lateral substituent would be expected to contribute to the molecular dissymmetry and possibly lead to a lower crystal-to-mesophase transition temperature. The lateral substituent would always lower the clearing temperature. Arora[5] prepared 4-alkoxybenzoates of hydroquinone and 2-methylhydroquinone, and found a decrease of 22° to 52 °C for the C–M transition temperature as a result of the lateral methyl substituent. A decrease in the clearing temperature was also obtained as expected. The mesomorphic ranges of the laterally substituted materials were depressed only slightly and in some cases increased relative to the unsubstituted analogs.

We have used lateral substitution in the phenyl 4-benzoyloxybenzoate system in the hopes of obtaining materials with lower C–M transition temperatures. Table 5 contains a list of some substituted 4-ethoxyphenyl 4-benzoyloxybenzoates with various lateral substituents. As a point of reference, we have prepared the unsubstituted member of this series, 4-ethoxyphenyl 4-benzoyloxybenzoate, (compound 4) which has a very short nematic range of 153–167 °C. The introduction of a 4-methyl group in ring *C* gave a liquid crystal (compound 8) with a nematic range of 150 °–257 °C which amounts to a 90° increase in the thermal stability of the nematic mesophase. This is a dramatic increase in both the nematic range and thermal stability as a result of what would seem at first glance to be a relatively small change in the molecular structure. In an effort to explain this increase, reference should be made to Dewar's work on the influence of *p*-phenylene groups in nematic liquid crystals.[9] He prepared liquid crystals in which one or more of the *p*-phenylene rings were replaced by bicyclo [2.2.2] octane or cyclohexane units. These structural changes decreased the mesomorphic thermal stability relative to the all phenyl system. The mesomorphic thermal stability of the liquid crystals containing the more flexible cyclohexane group was considerably lower than the stability of those containing the bicyclooctane group, thus pointing out the importance of a rigid linear geometry. The bicyclooctane

ring, although not as flat, was assumed to be equivalent to a benzene ring in terms of geometrical considerations. The importance of the π-electron system of the p-phenylene group in stabilizing the mesophase is apparent, since large decreases in nematic thermal stability were obtained as a result of the bicyclooctane substitution. However, the 90° increase in thermal stability of the mesophase, as a result of methyl substitution for compound 8 in Table 5, indicates that the

TABLE 5 Substituted 4-Ethoxyphenyl 4-Benzoyloxybenzoates

Ring Substituent						
A	*C*					Compound
R_4	R_2	R_3	R_4	Range (°C)	ΔT°	Number
OC_2H_5	H	H	H	153–167	14	4
OC_2H_5	H	H	CH_3	150–257	107	8
OC_2H_5	H	F	H	146–153	7	13
OC_2H_5	H	Cl	H	151–154 (120)	—	16
OC_2H_5	H	OCH_3	H	118–121[a]	—	11
OC_2H_5	H	H	OCH_3	144–284	140	5
OC_2H_5	OCH_3	H	OCH_3	144–171	27	12
OC_2H_5	H	H	Cl	149–258.5	109.5	10
OC_2H_5	Cl	H	H	124–127 (121)	—	14
OC_2H_5	Cl	H	Cl	119–205	86	15
OC_2H_5	H	Cl	Cl	145–189	44	17

[a] No mesophase detected.
( ) Monotropic transition.

π-electron system alone is not responsible for this increase; rather, it is a result of both the polarizability of the substituent itself and the electronic perturbations of the phenyl ring as a result of this substitution. The slight increase in length of the molecule as the result of methyl substitution is assumed to make a negligible contribution to the mesophase stability. Gray[10] has also mentioned the enhanced thermal stability of nematic mesophases resulting from p-substitution.

As the size of the lateral substituent increases, the thermal stability of the mesophase decreases. If the group is large enough, the mesomorphic character can be completely absent. The compounds containing fluoro, chloro, and methoxy substituents (compounds 11, 12 and 16 in Table 5) illustrate this point. Fluorine substitution would be the most desirable in terms of a smaller decrease in the N–I transition temperature; however, we have used

chlorine extensively as the lateral substituent because of the availability of the starting materials. The anticipated decrease in the C–M transition temperature as a result of the lateral substituent was found in the majority of cases. The equivalent C–M transition temperatures of compounds 5 and 12 are an example where the decrease was not obtained. Generally, as a given lateral substituent is located in different positions in the phenyl 4-benzoyloxybenzoate system, we have found greater differences in the C–M transition temperature than in the N–I transition temperature; compare compounds 14 and 16 in Table 5, which show a 27 ° difference in the C–M transition temperature and a 1 ° difference in the N–I transition temperature. Also, compare compounds 15 and 17 in Table 5, which show a 27 ° difference in the C–M transition and a 16 ° difference in the N–I transition. Since the classical nematic mesophase can be thought of as one structural type, i.e., a parallel arrangement of rod-shaped molecules, the larger differences in the crystal packing and cohesive forces in the solid state are normalized to a certain degree on passing into the nematic mesophase. This accounts for the smaller differences found for the N–I transition temperatures as compared with the differences in the C–M transition. The lowest crystal-to-mesophase transition temperatures are found when the chlorine substituent is adjacent to the carbonyl group of the ester function, as in compounds 15 and 17 in Table 5.

Some substituted 4-*n*-pentylphenyl 4-benzoyloxybenzoates are recorded in Table 6. The introduction of a lateral substituent does

TABLE 6 Substituted 4-*n*-Pentylphenyl 4-Benzoyloxybenzoates[a]

Ring Substituent					Nematic		Compound
B		*C*					
R_2	R_3	R_2	R_3	R_4	Range (°C)	$\Delta T°$	Number
H	H	H	H	OCH_3	87–223	136	40
H	H	Cl	H	OCH_3	109–168.5	59.5	52
H	H	H	H	OC_4H_9	89–209.5	120.5	41
H	H	H	H	$OCH_2CH(CH_3)_2$	110–179.5	69.5	42
H	H	H	H	C_5H_{11}	78–179.5	101.5	38
Cl	H	H	H	C_5H_{11}	39–122	83	49
H	Cl	H	H	C_5H_{11}	67–130	63	50

[a] All alkyl and alkoxy groups are normal unless otherwise indicated.

not always result in lower C–M transition temperatures, and in fact, can lead to relatively large increases, as in the 22 ° increase found for compounds 40 and 52 in Table 6.

Branching of the terminal alkoxy group as in compound 42, also resulted in an increase in the C–M transition temperature compared to the straight-chain derivative, compound 41; the N–I transition temperature was depressed by 30 °. This agrees with the recent work of Young,[11] who found no trend in the C–M transition temperatures for some branched alkyl derivatives of the stilbene class. He also found a 20–30 ° decrease in the N–I transition temperature as a result of methyl groups in the 2 or 3 position.

Compounds 49 and 50 in Table 6 are among the lowest melting materials that we have prepared in this series; their transition temperatures are 39–122 °C and 67–130 °C, respectively. Again, the compound with the lateral chloro substituent adjacent to the carbonyl group of the ester linkage gave the lowest melting material. Compound 49 has one of the broadest nematic ranges (83 °) for a single compound melting below 40 °C reported in the literature.

The additive nature of structural changes in decreasing the thermal stability of the nematic mesophase has been demonstrated by a number of workers. Gray[10] has shown that the decrease in thermal stability as a result of the introduction of several lateral substituents is approximately equal to the sum of the decreases obtained for each individual substituent. Similarly, Dewar[9] has found that the decrease in nematic thermal stability accompanying the replacement of *p*-phenylene groups by bicyclooctane groups is additive, that is, two groups have twice the effect of one group. We have been able to demonstrate this additivity effect in the liquid crystals prepared in this investigation. Table 7 contains a list of 4-*n*-pentylphenyl 4-chlorobenzoyloxybenzoates with one or more lateral chloro substituents. Compound 63 with two lateral chloro groups resulted in a decrease in the nematic thermal stability of 123 °C, relative to the control compound 46. This is very close to the sum (115.5 °) of the decreases for compounds 60 and 61, which have a single lateral substituent in an equivalent position. The agreement is even better for compound 64 (monotropic) with a decrease in thermal stability of 119 °; the sum of the decreases for the singly substituted compounds 60 and 62 is equal to 119.5 °.

Note that the largest difference in the N–I transition temperature for all the compounds in Table 7 with only one lateral substituent is only 5.5 °, whereas the largest difference in the crystal-to-mesophase transition temperature is 25 °. This trend has been referred to earlier in this paper and may serve as a rough guide in predicting the changes in the phase transition temperatures to be expected as a lateral substituent is located in different positions in compounds within a

TABLE 7 Additivity of Lateral Substituents
(Formula I where A–R_4 = n-C_5H_{11}; C–R_4 = Cl)

Ring Substituent							
B		*C*					
R_2	R_3	R_2	R_3	R_4	Mesophase Range (°C)[a]	Decrease in N–I from Compd. No. 40 (°C)	Compound Number
H	H	H	H	Cl	113S139–212	—	40
Cl	H	H	H	Cl	91–150	62	59
H	Cl	H	H	Cl	112–155	57	60
H	H	Cl	H	Cl	87–153.5	58.5	61
H	H	H	Cl	Cl	111S129–149.5	62.5	62
H	Cl	Cl	H	Cl	82–89	123	63
H	Cl	H	Cl	Cl	109–112 (93)	119	64

[a] Indicated range is nematic unless recorded as S for smectic.
( ) Monotropic transition.

series which have relatively similar terminal substituents. We might also expect that the differences in the transition temperatures would decrease, and the accuracy of the predictions, especially for changes in the clearing point, would increase as the terminal substituents become longer.

Comments regarding the effect of lateral substituents on the smectic phase are much more difficult to make in view of the multiplicity of smectic phases. The introduction of a lateral substituent into a liquid crystal which has both a smectic and a nematic phase can result in an increase in the nematic range, at the expense of the smectic phase; compare compounds 17 and 23 in Table 2.

During the course of this work, Young[12] has reported on the preparation of some phenyl 4-benzoyloxybenzoate liquid crystals

with lateral methyl substitution. The lowest crystal-to-mesophase transition temperature for one of these materials was 91 °C.

4. Conclusion

We have shown that liquid crystals of the phenyl 4-benzoyloxybenzoate class with terminal alkyl substituents and lateral chloro substituents can lead to materials with low crystal-to-mesomorphic transition temperatures and relatively broad ranges. Our future synthetic work will be a continuation of these approaches in order to obtain a further reduction in the crystal-to-mesophase transition temperatures.

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