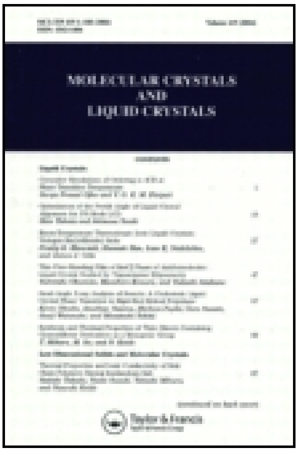

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The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Thiobenzoates 8. Phenylbenzoates Containing Two Carbonyl Containing Terminal Chains

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The Effect of Carbonyl Containing Terminal Chains on Mesomorphic Properties in 4,4′-Disubstituted Phenylbenzoates and Thiobenzoates 8. Phenylbenzoates Containing Two Carbonyl Containing Terminal Chains†

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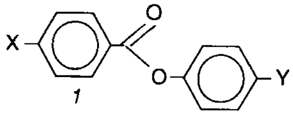
(Received October 30, 1992)

A variety of phenylbenzoates of the type



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with both X and Y being the carbonyl containing chains $(CH_2)_nCOR$ (n = 0 – 1), $(CH_2)_nCO_2R$ and $(CH_2)_nOCOR$ (R = alkyl chain) in various combinations were synthesized and their mesomorphic properties studied to determine if an additive effect occurs when these chains are incorporated into the same molecule. No reliable additive effect could be found. Instead, clearing temperatures often seemed to be closer to the clearing temperature of the parent single carbonyl containing chain ester with the higher clearing temperature. An attempt was also made to improve the properties of the esters *1* with X or Y being I, F, CN or NO_2 by using a carbonyl containing chain as the second substituent and assuming an additive effect. However, such an effect was also not observed in these esters. Smectic C phases were found in some of the esters with X = CN which is rare for compounds containing this substituent.

Keywords: liquid crystals, phenylbenzoates, synthesis, NMR, esters, ketones

INTRODUCTION

Earlier, we determined the mesomorophic properties for phenylbenzoates with one terminal chain having a carbonyl group and the other being a straight chain alkyl or alkoxy group *1*

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†Presented in part at the 14th International Liquid Crystal Conference, Pisa, Italy, 1992.

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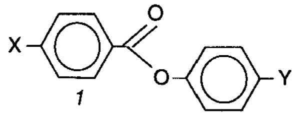

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	X	Y
a	R,RO	$(CH_2)_nCOR'$ n=0-2 [1,2]
b	R,RO	$(CH_2)_nCO_2R'$ n=0-2 [3]
c	R,RO	$(CH_2)_nOCOR'$ n=0-2 [4,5]
d	RCO	R', OR' [6]
e	RCO_2	R', OR' [7]

A comparison of the mesomorphic properties for these esters is shown in Figures 1–3. When either X or Y = COR, smectic A phases are favored at long chain lengths and transition temperatures are higher than when this chain is an alkyl group and independent of whether the other chain is an alkyl or alkoxy group (Figure 1). On the other hand, the effect of an acyloxy group on mesomorphic properties depends on both its location and whether the second chain is an alkyl or alkoxy group (Figure 2). Mesomorphic properties are better (more mesophases and/or wider phase ranges) for C_9CO_2—C_{10} than $C_{10}O$—C_{10} but are poorer for C_9CO_2—OC_{10} than for $C_{10}O$—OC_{10}. A similar trend can be seen where these properties are better for C_9CO_2—C_{10} than for C_{10}—$OCOC_9$ but poorer for C_9CO_2—OC_{10} than for $C_{10}O$—$OCOC_9$. Both trends illustrate the important role an ether linkage in the terminal chain on the acid side plays in determining these properties. Melting and clearing temperatures do not vary appreciably from the corresponding R/RO analogs. Clearing temperatures are a little higher when Y = $OCOC_9$ than when X = C_9CO_2 and polymorphism occurs with the presence of

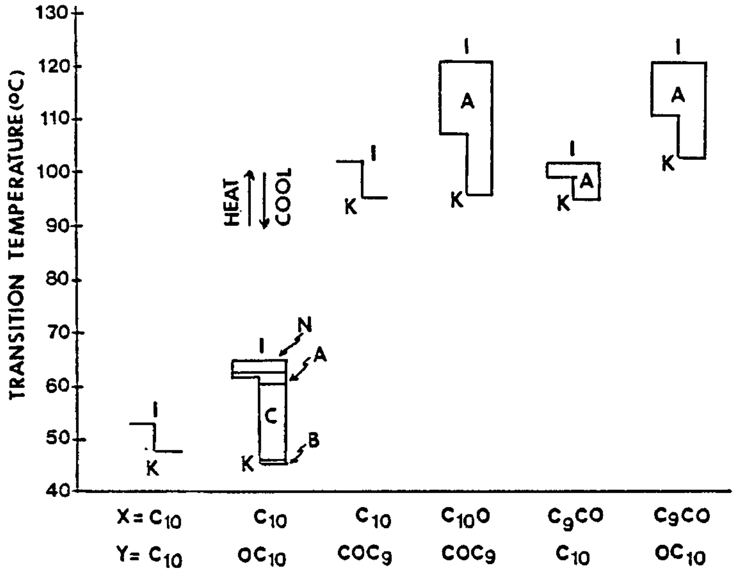
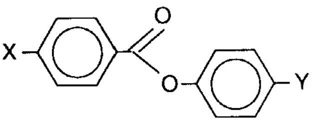


FIGURE 1 Transition temperatures for



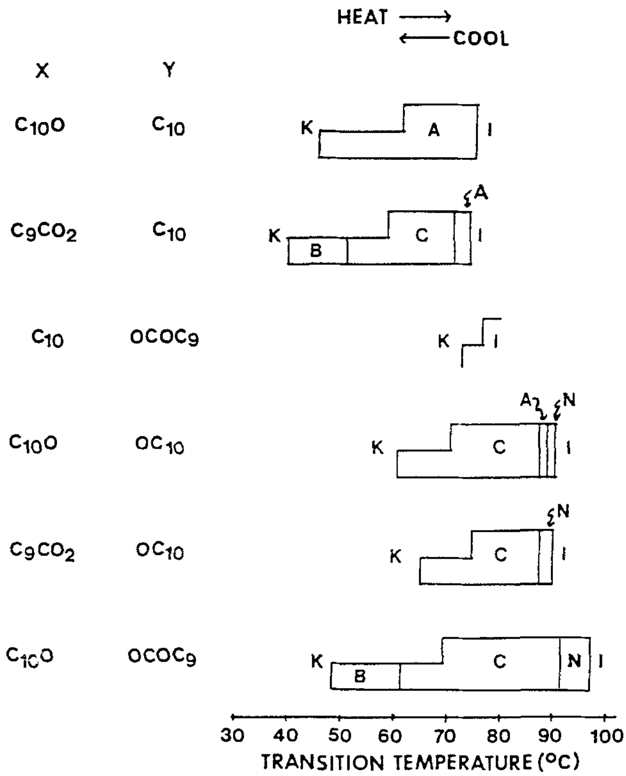
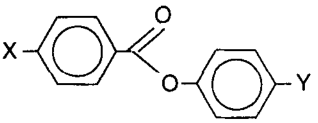


FIGURE 2 Transition temperatures for X



smectics B, C, A and nematic phases. The smectic B phase and sometimes the smectic C phase are enhanced.

Reversing the ester on the phenolic side* gives a preference for the smectic A phase and contrary to expectations, lowers transition temperatures when Y = CO_2C_9 (Figure 3). The addition of spacer methylene groups into these carbonyl containing chains usually gives lower transition temperatures and shorter mesophase ranges (Figure 3).

We were interested in determining if these effects of a single carbonyl containing chain on mesomorphic properties would show a quantitative additive effect when both X and Y are carbonyl containing chains. For example, could the tendency towards several mesophases and an enhanced smectic C phase which is observed when X = $C_{10}O$ and Y = $OCOC_9$ be combined with the higher temperatures and wider range smectic A phase when Y = COC_9 to give an ester with smectics B, C, A and a nematic phase over a wider temperature range? Although there is no good reason to believe this will be the case, there is the tendency to think it is true

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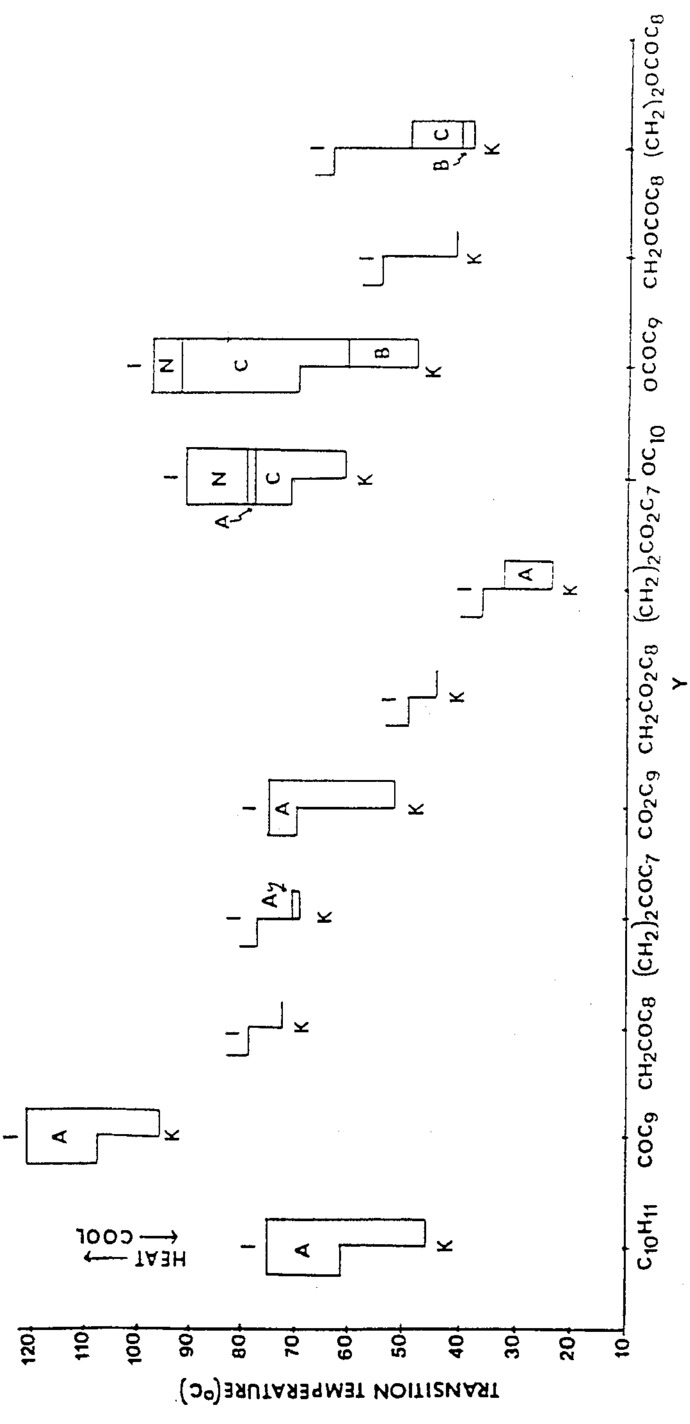
*Data are not yet available for a reversed ester chain on the acid side (X = ROCO).



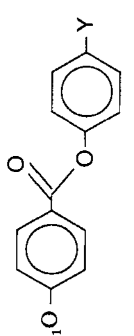
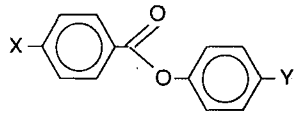


FIGURE 3 Transition temperatures for $C_{10}H_{21}O$

which then influences which structural modifications will be made in designing new liquid crystals. It would be very useful in this respect if it were indeed true.

To check the validity of this assumption, two different types of phenylbenzoates with carbonyl containing chain modifications were prepared. The first involved combining one of the carbonyl containing chains on the acid side with each of those previously studied on the phenol side to give the esters *2* and *3* with a minimal change in structural modification.

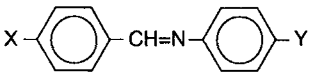


2 $X{=}C_9CO$

3 $X{=}C_9CO_2$

$Y{=}(CH_2)_nCOR', (CH_2)_nCO_2R', (CH_2)_2OCOR', O(CH_2)_nCO_2C_8$ and $O(CH_2)_nOCOC_7$

Although mesophases have been observed in the anils *4*



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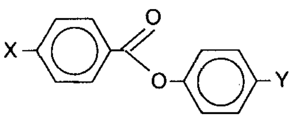
when X or Y is a halogen substituent,[8–12] none have yet been found in the halobenzoates. We were interested in trying to improve these properties by adding a carbonyl containing chain and at the same time checking the additive effect in esters in which a larger molecular modification was employed *5*, *6*.

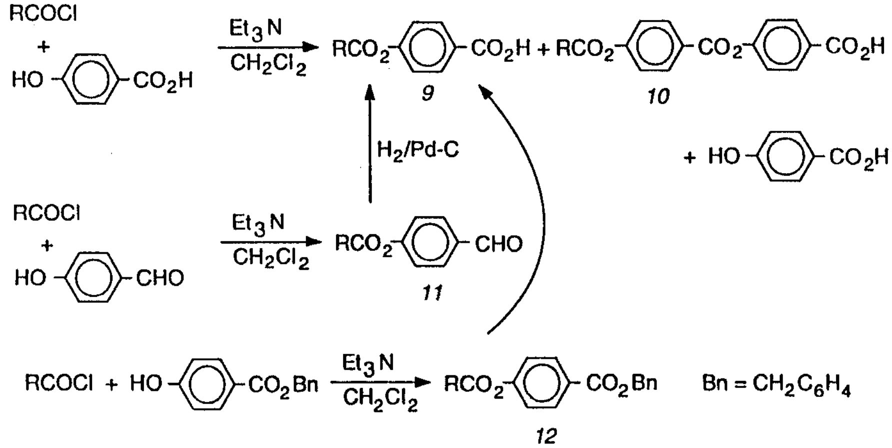


	X	Y
5	F,I	CO_9, CO_2C_9, $OCOC_9$
6	C_9CO, C_9CO_2	F
7	CN, NO_2	COC_9, CO_2C_9, OCOR
8	C_9CO, C_9CO_2	CN

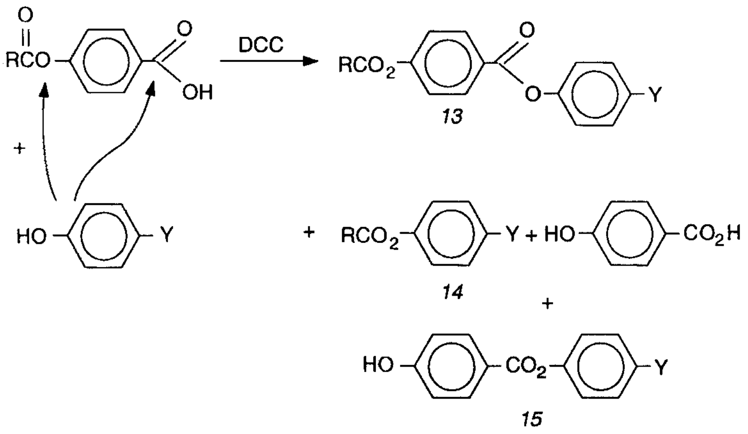
The esters with X or Y = CN or NO_2 *7* and *8* were also prepared since these were expected to have more mesophases and are particularly interesting because of their high polarity.

SYNTHESIS

All of these esters were prepared using the intermediates synthesized earlier for preparing the esters *1*. Some of the esters *3* were difficult to purify; a problem also encountered in the preparation of the esters *1b*, *c* and *e*. Purifying the acyloxy acid *9* (Scheme I) obtained by esterifying 4-hydroxybenzoic acid with an acid chloride proved difficult. We now believe this is due to esterification of the acid as well as the phenol to give the diester *10* along with 4-hydroxybenzoic acid, both of which are difficult to separate from the desired acid *8*. Earlier, this problem was avoided by going through the aldehyde *11*. In this paper, we isolated high-quality acid *9* by using the benzyl ester *12*. However, despite the use of good quality acid *9*,



SCHEME I



SCHEME II

purification of the phenylbenzoates having two carbonyl-containing chains with at least one of these being an ester acid was difficult. We now believe this is due to ester exchange giving a mixture of the esters *13*, *14* and *15* along with 4-hydroxybenzoic acid (Scheme II). Esterification seemed to proceed slowly in these cases so reaction times were increased. This only favored transesterification. Esters prepared in this manner often appeared to be pure by NMR after several recrystallizations and sometimes chromatography but showed a faint second spot near that of the desired ester on TLC plates. Determination of the transition temperatures by hot-stage polarizing microscopy, however, showed broad clearing temperatures; much wider than expected for the amount of impurity present. Careful flash chromatography (sometimes twice) on silica gel usually removed the impurity and gave a clearing temperature with a range of no more than 0.5°. We now feel that the impurity is probably the ester *14* resulting from transesterification or the ester resulting from esterification of the ester *15*. Such materials would be more likely to form a wide range liquid crystal phase in a mixture broadening the clearing temperature. The end of the clearing temperature range changed little with purification but the range decreased considerably. Once again this substantiates Gray's earlier comment that trace amounts of impurities have a larger effect on clearing than on melting temperatures.[13] In our experience, this is true but only when the impurity is similar enough in structure to the primary component to give a liquid crystal mixture with a broad clearing temperature. Transesterification did not seem to be a problem when the acid chloride method was used. Sharp clearing temperatures were obtained without chromatographic purification and this later became the method of choice.

The structure of all compounds were confirmed by IR and NMR. With our collective NMR knowledge about these compounds having carbonyl containing chains and use of a 200 MHz instrument to obtain both 1- and 2D-^{1}H spectra, it is possible to identify all the protons in the compounds prepared and use this as an accurate tool for identification and to some extent purity. From these collected data, we are now convinced that the order of chemical shifts for the aromatic protons ortho to carbonyl chains linked to the benzene ring through an oxygen atom compared to those ortho to an alkyl or alkoxy group is as follows:

$$\begin{aligned}&CH_2CO_2R(\text{phenol}) > OCORAr(\text{phenol with ews*}) > R(\text{acid}) \geqslant OCOR(\text{acid})\\ &\geqslant R(\text{phenol}) > OCOAr > OCOR(\text{phenol}) > OR(\text{acid}) > OR(\text{phenol})\end{aligned}$$

and the order of the protons ortho to the central ester carbonyl group and the terminal carbonyl containing chains connected through the carbonyl carbon atom is as follows:

$$CO_2AR \geqslant CO_2R(\text{phenol}) > RCO(\text{acid}) > RCO(\text{phenol}).$$

Abbreviated NMR data of typical examples are provided in the experimental section for use as future reference standards.

MESOMORPHIC PROPERTIES

Transition temperatures (°C) for all the esters prepared were determined by hot-stage polarizing microscopy and are given in Tables I–III. Some previously reported data for known esters used for comparison are also included in Table III along with some new standard esters.

To determine if an additive effect occurred in the transition temperatures for the esters with two carbonyl containing chains *2* and *3*, predicted transition temperatures were determined by averaging the data for each parent compound (e.g., the melting temperatures for $X = C_{10}$, $Y = COC_9 = 101.8$ and for $X = C_9CO$, $Y = C_{10} = 98.8$ and the average is 100.3). The difference between this value and the oberved temperature for the new ester is given in the APMT and APCT columns of Tables IV and V. Rarely does this difference show a quantitative additive effect.

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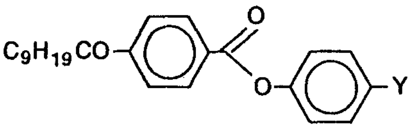
*ews = electron withdrawing substituent.

Usually the observed temperatures are much higher. That these differences have primarily positive values suggest that the predictions are poor. Therefore, predicted values were also determined by calculating the difference between each mono carbonyl containing chain ester from its corresponding alkyl/alkoxy ester, adding these two differences to obtain the total difference for the ester with two carbonyl containing chains and adding this total to the transition temperature for the R/OR standard ($X = Y = C_{10}$ for the above example). This gave newly predicted values DPMT and DPCT in Tables IV and V. Differences between these values and those observed are smaller and show both negative and positive values but are still too large to suggest a reliable quantitative additive effect. In a number of cases, the observed transition temperature was closer to that observed for the mono carbonyl containing chain component having the highest transition temperature (HCMT and HCCT).[1] This is particularly true of the clearing temperatures.

Transition temperatures were predicted in the same manner for the many known alkyl/alkoxy phenylbenzoates where a large number of compounds are available[17] and the structural modifications are smaller. Twenty-nine dialkoxy esters were compared with the various R/OR combinations. Again no reliable quantitative additive effect could be found. In all these calculations, occasionally the predicted

TABLE I

Transition temperatures (°C) for



Y	K[a]	A	I
COC_9H_{19}	141.7	144.7-145.4	148.8-149.7
$CH_2COC_8H_{17}$	131.7		134.7-134.9
$(CH_2)_2COC_7H_{15}$	112.7		119.1-119.2
$CO_2C_9H_{19}$	87.8[b]	96.4-97.3	105.0-105.4
$CH_2CO_2C_9H_{19}$	106.4		109.6-111.3
$(CH_2)_2CO_2C_7H_{15}$	65.5		68.0-70.0
$(CH_2)_2CO_2C_9H_{19}$	70.2 K_1 68.1 K_2		72.0-73.0 (K_1) 71.3-71.7 (K_2)
$OCH_2CO_2C_8H_{17}$	82.4		88.9-89.7
$OCOC_9H_{19}$	127.6	(127.9)[c]	134.8-135.2
$O(CH_2)_2OCOC_7$	101.8		104.9-105.2

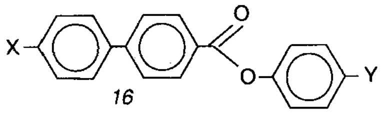
a. K=crystallization temperature obtained on cooling the melt at 2°/min, A=smectic A phase and I=isotropic liquid and ( ) indicates a monotropic phase. Procedural details are given in the experimental section.

b. These crystals changed to another crystalline form at 94.5-95.5° on reheating which then melted to the A phase.

c. This temperature was obtained on cooling since the sample crystallized too rapidly to reheat the A phase.

values come close to the actual values but this trend does not continue for a large number of comparisons. Obviously none of these methods are useful in predicting transition temperatures.

Mesophases were also compared with those predicted based on the properties of the mono carbonyl containing chains (Table VI). Again no quantitative additive effect was observed. In some instances the mesophase range increases rather than decreases; in others the decrease is greater than predicted. When monotropic phases are predicted and none were observed, it is difficult to say the prediction is inaccurate since the observance of these phases depends on the crystallization temperature. In choosing the phenylbenzoates to study this effect, we expected to observe better mesophase ranges. These esters offered a better approach for preparing a large number of chain modifications than the substituted biphenyls. In retrospect, a better series to study would probably have been the biphenyl esters *16*



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which would more likely have shown more enantiotropic phases.

Combining a carbonyl containing chain with a halogen atom was equally disappointing (Table III). Mesomorphic properties did not improve when an alkyl or alkoxy chain on either the acid or phenol side were replaced by a carbonyl containing chain. With the strong smectic A enhancement observed in the alkyl/alkoxy esters when X or Y = COC_9, it seemed likely that a smectic A phase would occur when the other chain was a halogen atom but none was observed. The order of melting temperatures was as follows:

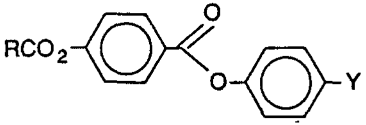
$$Y = COC_9 > OCOC_9 > OC_{10} > CO_2C_9$$

again showing lower melting temperatures for Y = CO_2C_9 than for $OCOC_9$; the opposite expected from dipole moments consideration.

Good mesomorphic properties were observed in many of the esters with X or Y = CN or NO_2, perhaps because they can form bilayers. More mesophases seem to occur when the polar substituent is on the acid rather than the phenolic side. In the ester with X = CN and Y = COC_9, a smectic A phase occurs but it is weaker than when Y = C_{10} although the expected higher transition temperatures were observed. Interestingly, a smectic C phase was also seen. Both smectics A and C phases occurred when X = CN and Y = OR. Replacement of the OR group with the $OCOC_9$ group did not give an enhanced smectic C phase as expected but both smectic A and nematic phases. Thus the effect of Y = COC_9 and $OCOC_9$ is the opposite of that expected from studies with the esters containing these chains and X = RO. The esters with Y = COC_9 and OR represent the only known compounds with a strong dipole along the molecular axis that have a smectic C phase that we are aware of. It is obvious simply by looking at these data that an additive effect also does not occur in these esters.

TABLE II

Transition temperatures (°C) for



R	Y	K[a]	C	A	N	I
C_7CO_2	COC_7H_{15}	100.2	- - -	116.5-116.6	- - -	123.6-123.9
	COC_9H_{15}	102.3	- - -	113.0-114.2	- - -	124.6-124.9
	$CO_2C_9H_{15}$	31.8		51.4-51.9	- - -	65.8-66.3
	$OCOC_4H_9$	71.7	- - -	- - -	82.6-83.5	102.1-102.3
	$OCOC_9H_{19}$	82.8	86.4-87.5	- - -	90.8-91.2	100.7-101.1
$C_9H_{19}CO_2$	COC_4H_{19}	90.1	- - -	102.7-102.9	- - -	123.2-123.4
	COC_9H_{19}	107.0	- - -	116.1-118.2	- - -	126.0-126.5
	$CH_2COC_8H_{17}$	79.9	- - -	- - -	- - -	88.7-89.0
	$(CH_2)_2COC_7H_{15}$	84.4[b] (K_2)		- - -	- - -	85.6-86.4 (K_2) 90.0-90.8 (K_1)
	$CO_2C_9H_{19}$	42.6		63.4-63.7		73.0-73.3
	$CH_2CO_2C_9H_{19}$	54.7[c]				63.3-64.8
	$(CH_2)_2CO_2C_7H_{15}$	35.1[d] (K_3)				44.4-45.8 (K_2) 46.4-47.7 (K_1)
	$OCOC_4H_9$	72.2	- - -	- - -	86.9-87.0	94.9-95.2
	$OCOC_7H_{15}$	85.3	(92.9-93.4)		93.2-93.7	100.6-100.8

	$OCOC_9H_{19}$	89.2	96.5-96.8	- - -	101.1-101.3	102.0-102.1
	$(CH_2)_2OCOC_8H_{17}$	65.8				69.1-70.1
$C_{11}H_{23}CO_2$	COC_9H_{19}	90.0	(101.1-106.6)	113.0-113.3	- - -	124.1-124.5
	$CO_2C_9H_{19}$	45.5-42.9[e]		66.0-66.9	- - -	76.5-77.1
	$OCOC_9H_{19}$	87.5	94.5-95.1			104.4-104.6

a. K=temperature at which crystallization occurs on cooling the melt at 2°/min, C=smectic C, A=smectic A, N=nematic and I=isotropic liquid and ( ) indicates monotropic transition.Procedural details are given in the experimental section.

b. Further cooling gave another crystal form (K_1) at 79.0°.

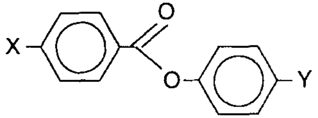
c. These crystals changed to another form on reheating at 60.7-62.5°.

d. Further cooling gave two more crystal forms at 34.5° (K_2) and 32.0° (K_1).

e. Bright crystals grow slowly at first, then suddenly most of these change to a black mosaic texture at ~40.7°. These become brighter on further cooling. These were reheated to give the melting temperature.

TABLE III

Transition temperatures (°C) for



R	Y	K[a]	S	C	A	N	I
F	$C_{10}H_{21}$	60.4					64.0-64.9
	COC_9H_{19}	118.9					122.3-122.4
	$CO_2C_9H_{19}$	50.1					66.8-68.6
	$OC_{10}H_{21}$	78.7					75.5-83.4[b]
	$OCOC_9H_{19}$	90.5					93.5-94.2
I	$C_{10}H_{21}$	86.3					90.4-91.5
	COC_9H_{19}	142.0					148.1-148.4
	$CO_2C_9H_{19}$	70.3					80.5-80.6
	$OC_{10}H_{21}$	113.3					116.3[b]
	$OCOC_9H_{19}$	133.2					135.2-137.2
$C_{10}H_{21}$	F	27.7					55.3-55.5
$C_9H_{19}CO$	F	120.7					124.7-124.9
$C_{10}H_{21}O$	F	41.6			(46.3)		64.6-65.0[b]
$C_9H_{19}CO_2$	F	53.3					65.5-65.9
NC	$C_{10}H_{21}$	51.3[c]			66.0-66.4	- - -	81.2-81.6
	COC_9H_{19}	100.5		106.3-107.5	112.6	- - -	113.0-113.2

	$CO_2C_9H_{19}$	49.3				(60.6-61.1)	63.9-65.1
	OC_9H_{19}	55.6		(55.7)	69.2-70.3	- - -	96.0-96.3[d]
	$OC_{10}H_{21}$	55.0		(61.2-61.4)	67.4-68.6	- - -	100.9-101.3[d]
	$OCOC_7H_{15}$		74				99.5[e]
	$OCOC_9H_{19}$	76.4			81.9-82.1	102.0-102.1	105.6-105.8
$C_{10}H_{21}$	CN	34.6			(56.2-56.3)	59.4-60.4	60.7-60.9
$C_9H_{19}CO$	CN	111.1					114.0-114.8
$C_{10}H_{21}O$	CN				(78)	79	86[f]
$C_9H_{19}CO_2$	CN	60.8			66.6-67.1	73.4-73.8	86.6-87.0
O_2N	$C_{10}H_{21}$	31.4			41.9-42.4		58.5-59.0
O_2N	COC_9H_{19}	61.5			(71.8)	(77.8)	88.5-89.5
O_2N	$CO_2C_9H_{19}$	40.9					57.8-58.8
O_2N	OC_9H_{19}		69				78[e]
O_2N	$OCOC_9H_{19}$	64.3[g]			70.2-70.5 (K_1)	88.8-88.9	91.4
$C_{10}H_{21}O$	NO_2	34			53.6		76.9[b]

a. K=crystallization temperature obtained on cooling the melt at 2°/min, S=unidentified smectic phase, C=smectic C and A=smectic A, N=nematic phases and I=isotropic liquid. ( ) indicates a monotropic phase. Procedural details are provided in the experimental section.

b. Data are from reference 8.

c. A crystal-to-crystal transition occurs at 49.2° on further cooling. This second crystal form melts to the smectic A phase on reheating.

d. Our data agree with those reported by R. Hopf in reference 14.

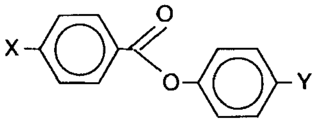
e. Data are from reference 15.

f. Data are from reference 16.

g. A second crystal form (K_2) was observed on further cooling at 64.3°. On reheating these converted back to K_1 at 68.2-68.9° and then melted to the A phase on further heating.

TABLE IV

Comparison of actual with predicted melting temperatures (°C) for



X	Y	Difference from APMT[a]	Difference from DPMT[b]	Difference from HCMT[c]
C_9CO	COC_9	45.1	-2.4	43.6
	CH_2COC_8	41.2	12.7	36.1
	$(CH_2)_2COC_7$	33.2	0	20.4
	CO_2C_9	13.0	-21.9	-1.5
	$CH_2CO_2C_9$	40.6	NED[d]	12.5
	$(CH_2)_2CO_2C_7$	7.2	49.2	-28.8
	$OCOC_9$	41.4	9.6	25.1
C_9CO_2	COC_4	26.9	17.5	10.3
	COC_9	35.0	13.4	10.6
	CH_2COC_8[e]	20.4	13.3	10.5
	$(CH_2)_2COC_7$	22.8	16.5	13.7
	CO_2C_9	-0.4	2.6	-5.4
	$(CH_2)_2CO_2C_7$[e]	0.1		-11.2
	$OCOC_4$	20.6	17.5	19.7
	$OCOC_7$	23.1		20.1
	$OCOC_9$	24.8		22.1

a. APMT=averaged predicted melting temperature; obtained by averaging the melting temperatures for the two known monocarbonyl containing chain standards.

b. DPMT=difference predicted melting temperature obtained by determining the difference between melting temperatures for each component and a corresponding R/RO standard, adding these to obtain the total difference and then adding these to the R/RO standard. Data for the R/RO standards were taken from reference 17.

c. HCMT=melting temperature of the highest standard with only one carbonyl containing chain.

d. NED = not enough data for standards.

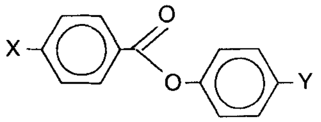
e. Chain lengths compared are not exactly the same.

CONCLUSIONS

A reliable additive effect in both the transition temperatures and mesomorphic properties in these esters was not observed either in a qualitative or quantitative sense. At times, a qualitative effect seems to occur. An α-keto group often increases transition temperatures and gives a smectic A phase. However, in other instances, no smectic A phase occurs but instead a smectic C phase is seen. The unreliability of even the qualitative trends is obvious in the series with X = CN. This supports

TABLE V

Comparison of actual with predicted clearing temperatures (°C) for



X	Y	Difference from APCT[a]	Difference from DPCT[b]	Difference from HCCT[c]
C_9CO	$OCOC_9$	31.3	-0.7	7.5
C_9CO_2	COC_4	29.4	37.7	2.8
	COC_9	29.1	20.3	5.8
	CO_2C_9	-1.1	-0.4	-1.4
	$OCOC_4$	6.3	2.2	1.1
	$OCOC_7$	8.6		5.9
	$OCOC_9$	8.5		5.3
$C_{11}CO_2$	$OCOC_9$	9.1		6.9

a. APCT=averaged predicted clearing temperature obtained by averaging the melting temperatures for the two monocarbonyl containing chain standards.

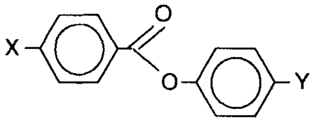
b. DPCT=difference predicted clearing temperature obtained by determining the difference between clearing temperatures for each monocarbonyl containing chain standard and the corresponding R/RO standard, adding these differences to obtain the total difference and then adding this total to the clearing temperature for the R/RO standard. Data for the R/RO standards were taken from reference 17.

c. HCCT=clearing temperature for the monocarbonyl containing chain standard with the highest clearing temperature.

the idea that mesomorphic properties are determined by a combination of molecular properties such as dipole moments, polarizability, chain configuration and molecular shape. Although in some compounds, the influence of one of these properties may be enough to determine mesomorphic properties, in most cases more than one factor is involved, making each structure a unique one in how the molecules pack and determine which mosomorphic properties will be observed. Despite the large number of liquid crystals that have been synthesized, we can still only guess at what mesomorphic properties will be observed for a specific compound. Sometimes the guess is a good one, whereas at other times it is not. Even when theory is combined with known structure-property relationships to design a new liquid crystal, the result may be a compound that simply melts to an isotropic liquid and crystallizes on cooling. However, nothing is gained by not trying. From our studies on the effect of carbonyl containing chains, we have learned that the flexibility of a terminal chain can be as important as the chain length or dipole moment in determining mesomorphic properties which is also supported by recent studies on esters containing fluorinated chains.[18]

TABLE VI

Comparison of observed mesophases with those predicted for



X	Y	Predicted[a]	Observed[b]
C_9CO	COC_9	A	A↑[b]
	CH_2COC_8	A	none
	$(CH_2)_2COC_7$	A	none
	CO_2C_9	A	A
	$CH_2CO_2C_9$	(A)	none
	$(CH_2)_2CO_2C_7$	A	none
	$(CH_2)_2CO_2C_9$	A	none
	$OCH_2CO_2C_8$[c]	A	none
	$OCOC_9$	A,(N)	(A)
	$(CH_2)_2OCOC_8$[c]	A	none
C_7CO_2	COC_7	A,C,N	A↓,C,N
	COC_9	A,C,N	A
	CO_2C_9	C,N	A
	$OCOC_9$	C,N	C,N
C_9CO_2	COC_4	(B),(C),A,N	A
	COC_9	(B),C,A	A
	CH_2COC_8	(B),C,A	none
	$(CH_2)_2COC_7$	(B),C,A	none
	CO_2C_9	B,C,A	A↑
	$CH_2CO_2C_8$	(B),C,A	none
	$CH_2CO_2C_9$	B,C,A	none
	$(CH_2)_2CO_2C_7$	no B,C,A	none
	$OCOC_4$	B,C,N	N↓
	$OCOC_7$	no B,C,N	C↓,N↓
	$OCOC_9$	no B,C,N	C↓,N↓
$C_{11}CO_2$	COC_9[c]	no B,C,A	(C),A↑
	CO_2C_9[c]	(C),A	A↑
	$OCOC_9$	B,C,(N)	C↓

a. B,C and A are smectic phases with these identifications; N=nematic phase.

b. ↓ phase is shorter range than predicted, ↑ phase has a longer range than predicted.

c. Data available for only one standard needed in this comparison. Mesophases predicted are the minimal ones expected.

EXPERIMENTAL

All compounds prepared in this work were purified until they showed only one spot by TLC. Most of the phenylbenzoates were prepared using the carbodiimide esterification method[4] and recrystallized three times from abs EtOH. A few (X or Y = ester group) were prepared using the acid chloride method[5] which gave purer material. Purity was checked by TLC on Anal-Tech silica gel GHLF Uniplates using UV light and I_2 as the detectors and $CHCl_3$ as the solvent. When more than one spot was observed, these materials were purified further using flash chromatography[19] on Aldrich grade 60 (mesh 230–400) silica gel eluting with CH_2Cl_2-hexane mixtures followed by recrystallization from abs EtOH until clearing temperature ranges were <0.5°.

Melting points were determined using a Hoover-Thomas melting point apparatus unless otherwise noted and are corrected. IR spectra were obtained in Nujol on a Pye Unicom 3-200 instrument. Most of the NMR spectra were run on a Varian Gemini 200 instrument; a few were determined using a Varian FT80 (FT) or General Electric 300 (GE) instrument. All were run in $CDCl_3$ using TMS as the internal standard. The Gemini 200 gave better resolution of peaks than previously observed on the EM360 and therefore some data may differ slightly from those previously reported for the mono carbonyl chain esters which were used as standards for comparison. Also there are a few changes in assignments based on the new data. NMR data for the R/OR esters previously reported[20] were also used in these comparisons.

Transition temperatures (°C) were determined using a Leitz-Laborlux 12 Pol polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage at a heating rate of 2°/min as previously described.[15] Samples were cooled at 2°/min until they crystallized to obtain the crystallization temperature and so that no monotropic phases occurring before this temperature were missed. Temperatures for monotropic phases were obtained by reheating these phases and were identified as monotropic by the fact that they occurred below the melting temperature. Mesophases were identified by the observance of the textures typical of these phases as previously described.[21–23]

4-Benzyloxybenzoic Acid

Alkylation of 4-hydroxybenzoic acid methyl ester with benzylbromide was done using the DMF benzene method.[24] Hydrolysis of the ester in basic EtOH—H_2O was facilitated by the addition of THF (20 ml/0.13 mole) and additional H_2O (20 ml) to make stirring easier. The reflux time was 21–24 hr. The primary problem in purifying this acid seemed to be the presence of the less soluble acid salt despite acidification during workup. When the precipitate from acidification was stirred in warm glac HOAc, filtered, washed with H_2O and dried, the salt-free acid was isolated. Recrystallizations could then be done using abs EtOH to give high quality 4-benzyloxybenzoic acid with mp 187–190°. For characterization data see Reference 3.

Nonyl-4-hydroxybenzoate

The DMF-benzene alkylation method[24] was used to esterify 4-benzyloxybenzoic acid with 1-bromononane to give nonyl-4-benzyloxybenzoate in a yield of 34.0%

after recrystallization from abs EtOH twice m.p. 39–41° (lit.[3] m.p. = 42.0–44.0°). Hydrogenolysis gave the phenol in a yield of 65.4% after purification by flash chromatography (silica gel, 10% hexane in CH_2Cl_2) followed by recrystallization from abs EtOH (m.p. 43–44°).

4-Nonanoyloxybenzoic Acid *9* (R = C_9H_{19})

To a stirred solution of 4-hydroxybenzoic acid benzyl ester* (50.0 g, 0.22 mole) and Et_3N (96.6 ml) in CH_2Cl_2 (242 ml) was added dropwise nonanoyl chloride (41.9 g, 0.22 mole). After refluxing for 1.5 hr, the reaction mixture was extracted with H_2O, 5% aq KOH and H_2O. The organic layer was dried over anhyd Na_2SO_4, filtered and the filtrate rotovaped to give 79.0 g (98.3%) of the crude ester. Purification of this material by flash chromatography on silica gel eluting with 60% CH_2Cl_2 in hexane gave 75.6g (89.8%) of the purified liquid ester *12* (R = C_9H_{19}): TLC (R_f = 0.53); IR (film) 1760, 1720 (str, CO_2C_9 and CO_2Bn, respectively) and 1600 cm^{-1} (str, Ar) and NMR 8.10 (d, 2, J = 8.79 Hz, ArH ortho to CO_2Ar), 7.48–7.32 (m, 5, ArH ortho to CH_2), 7.15 (d, 2, J = 8.71 Hz, ArH ortho to $OCOC_9$), 5.35 (s, 2, $ArCH_2$) 2.56 (t, 2, J = 7.47 Hz, $OCOCH_2$), 1.75 (quint, 2, J = 7.2 Hz, $O_2CCH_2\underline{CH_2}$), 1.35–1.21 (m, 12, $6CH_2$) and 0.88 (t, 3, J = 6.45 Hz, CH_3).

A solution of this material (15.0 g, 0.04 mole) in abs EtOH (200 ml) containing 10% Pd/C (410 mg) was hydrogenated at 50 lb/in.^{2} at room temperature for 1 hr. Removal of the catalyst by filtration over Celite on glass fiber filter paper and rotovaping the filtrate gave 7.9 g (69.2%) of the crude acid. Recrystallization of this material twice from abs EtOH gave 7.1 g (60.5%) of the purified acid *9* (R = C_9H_{19}): mp 140–142°; IR 1740 (med, CO_2R), 1700 (med CO_2H) and 1600 cm^{-1} (wk, Ar) and NMR 8.15 (d, 2, J = 8.46 Hz, ArH ortho to CO_2H), 7.21 (d, 2, J = 8.63 Hz, ArH ortho to O_2CC_9), 2.59 (t, 2, J = 7.47 Hz, $O_2C\underline{CH_2}$), 1.77 (quint, 2, J = 6.96 Hz, $O_2CCH_2\underline{CH_2}$), 1.52–1.18 (m, 12, $6CH_2$) and 0.89 (t, 3, J = 6.33 Hz, CH_3).

Summary of IR Spectra Data for the Esters *2, 3, 5–7*

In Nujol, a weak aromatic absorption usually occurred between 1610 and 1590 cm^{-1}. Nitrile peaks were often not observed in Nujol but gave weak absorptions at ca. 2200 cm^{-1} in $CHCl_3$. The absence of nitrile peaks in aromatic compounds containing oxygen atoms is not unusual.[26] The ester carbonyl absorptions were usually resolved in 2–3 peaks (depending on the number present) between 1760 and 1720 cm^{-1} sometimes occurring as a shoulder while the ketone carbonyl absorptions appeared between 1665 and 1710 cm^{-1} as expected. The ester peaks were better resolved in Nujol than in $CHCl_3$. Undoubtedly better resolution could be obtained on a higher quality instrument. When X or Y = C_9CO_2 and the other terminal substituent is F, an additional splitting of the ester peaks occurred in Nujol but not in $CHCl_3$.

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*Purchased from TCI American.

NMR Spectral Data—Typical Examples for Esters 2, 3, 5–7

Terminal chain methylene groups beyond the second one from the carbonyl group appeared in all these esters as a multiplet between 2.0 and 1.1δ and the end methyl group occurred as a triplet at 0.88δ with J = 5.3–6.6 Hz. Data for the remaining protons are given in the following order: chemical shift (δ), multiplicity, number of protons, J (Hz) and identification. Only primary splittings are recorded.

$\underline{\mathrm{X = C_9CO,\ Y = COC_9}}$ too insoluble to obtain a spectrum; $\underline{\mathrm{Y = CH_2COC_8}}$ (FT), 8.28 (d, 2, 8.6, ArH ortho to $\mathrm{CO_2Ar}$), 8.04 (d, 2, 8.5, ArH ortho to $\mathrm{C_9CO}$), 7.23 (s, 4, ArH ortho to $\mathrm{CH_2}$ and OCOAr), 3.70 (s, 2, $\mathrm{Ar\underline{CH_2}COC_8}$), 2.99 (t, 2, 7.5, $\mathrm{CH_2COAr}$) and 2.47 (t, 2, 7.2, $\mathrm{CO\underline{CH_2}C_7}$); $\underline{\mathrm{Y = (CH_2)_2COC_7}}$ 8.27 (d, 2, 8.71, ArH ortho to $\mathrm{CO_2Ar}$), 8.06 (d, 2, 8.75, ArH ortho to $\mathrm{COC_9}$), 7.26 (d, 2, 8.71, ArH ortho to $\mathrm{CH_2}$), 7.13 (d, 2, 8.67, ArH ortho to OCOAr), 3.02 (t, 2, 7.34, $\mathrm{C_8\underline{CH_2}CO}$), 2.93 (t, 2, 7.37, $\mathrm{ArCH_2}$), 2.75 (t, 2, 6.84, $\mathrm{CH_2COC_7}$), 2.40 (t, 2, 7.37, $\mathrm{CO\underline{CH_2}C_6}$), 1.76 (t, 2, 7.12, $\mathrm{COCH_2\underline{CH_2}C_7}$) and 1.70–1.50 (m, 2, $\mathrm{COCH_2\underline{CH_2}C_5}$); $\underline{\mathrm{Y = CO_2C_9\ (GE)}}$ 8.28 (d, 2, 7.78, ArH ortho to $\mathrm{CO_2Ar}$), 8.14 (d, 2, 7.57, ArH ortho to $\mathrm{CO_2C_9}$), 8.08 (d, 2, J = 7.11, ArH ortho to $\mathrm{COC_9}$), 7.32 (d, 2, 7.26, ArH ortho to OCOAr), 4.33 (t, 2, 6.36, $\mathrm{CO_2CH_2}$), 3.02 (t, 2, 6.85, $\mathrm{C_8\underline{CH_2}CO}$) and 1.80–1.76 (m, 4, $\mathrm{CO_2CH_2\underline{CH_2}}$ and $\mathrm{C_7\underline{CH_2}CH_2CO}$); $\underline{\mathrm{Y = CH_2CO_2C_8}}$ 8.28 (d, 2, 8.05, ArH ortho to $\mathrm{CO_2Ar}$), 8.07 (d, 2, 8.38 ArH ortho to $\mathrm{COC_9}$), 7.37 (d, 2, 8.51, ArH ortho to $\mathrm{CH_2}$), 7.19 (d, 2, 8.56, ArH ortho to OCOAr), 4.10 (t, 2, 6.71, $\mathrm{CO_2CH_2}$), 3.64 (s, 2, $\mathrm{ArCH_2CO_2}$), 3.02 (t, 2, 7.34, $\mathrm{C_8\underline{CH_2}CO}$), 1.80–1.70 (m, 2, $\mathrm{CO_2CH_2\underline{CH_2}C_6}$) and 1.70–1.50 (m, 2, $\mathrm{C_7\underline{CH_2}CH_2CO}$); $\underline{\mathrm{Y = (CH_2)_2CO_2C_9}}$ 8.28 (d, 2, 8.67, ArH ortho to $\mathrm{CO_2Ar}$), 8.07 (d, 2, 8.67, ArH ortho to $\mathrm{COC_9}$), 7.28 (d, 2, 8.06, ArH ortho to $\mathrm{CH_2}$), 7.14 (d, 2, 8.51, ArH ortho to OCOAr), 4.08 (t, 2, 6.68, $\mathrm{CO_2CH_2}$), 3.02 (t, 2, 7.20, $\mathrm{C_8\underline{Ch_2}CO}$), 2.98 (t, 2, 7.00, $\mathrm{ArCH_2}$, 2.65 (t, 2, 7.68, $\mathrm{CH_2CO_2C_9}$), 1.85–1.70 (m, 2, $\mathrm{CO_2CH_2\underline{CH_2}}$) and 1.70–1.50 (m, 2, $\mathrm{C_7\underline{CH_2}CH_2CO}$); $\underline{\mathrm{Y = OCH_2CO_2C_8}}$ 8.27 (d, 2, 8.58, ArH ortho to $\mathrm{CO_2Ar}$), 8.06 (d, 2, 8.63, ArH ortho to $\mathrm{COC_9}$), 7.16 (d, 2, 9.16, ArH ortho to OCOAr), 6.97 (d, 2, 9.15, ArH ortho to $\mathrm{OCH_2}$), 4.64 (s, 2, $\mathrm{ArOCH_2}$), 4.22 (t, 2, 6.70, $\mathrm{CO_2CH_2}$), 3.02 (t, 2, 7.34, $\mathrm{COCH_2}$) and 1.85–1.60 (m, 4, $\mathrm{C_7\underline{CH_2}CH_2CO}$ and $\mathrm{CO_2CH_2\underline{CH_2}C_6}$); $\underline{\mathrm{Y = OCOC_9}}$ 8.28 (d, 2, 8.67, ArH ortho to $\mathrm{CO_2Ar}$), 8.09 (d, 2, 8.67, ArH ortho to $\mathrm{C_9CO}$), 7.25 (d, 2, 9.08, ArH ortho to OCOAr), 7.15 (d, 2, 9.32, ArH ortho to $\mathrm{OCOC_9}$), 3.02 (t, 2, 7.34, $\mathrm{C_8CH_2CO}$), 2.57 (t, 2, 7.48, $\mathrm{OCOCH_2}$) and 1.76 (quint, 4, 7.14, $\mathrm{OCOCH_2\underline{CH_2}}$ and $\mathrm{C_7\underline{CH_2}CH_2CO}$); $\underline{\mathrm{Y = O(CH_2)_2OCOC_7}}$ 8.27 (d, 2, 8.43, ArH ortho to $\mathrm{CO_2Ar}$), 8.06 (d, 2, 8.46, ArH ortho to $\mathrm{COC_9}$), 7.15 (d, 2, 8.95, ArH ortho to OCOAr), 6.96 (d, 2, 9.15, ArH ortho to $\mathrm{OCH_2}$), 4.43 (t, 2, 4.72, $\mathrm{ArOCH_2}$), 4.18 (t, 2, 4.72, $\mathrm{ArOCH_2\underline{CH_2}O}$), 3.02 (t, 2, 7.33, $\mathrm{COCH_2}$), 2.36 (t, 2, 7.49, $\mathrm{OCOCH_2}$) 1.76 (quint, 2, 7.18, $\mathrm{COCH_2\underline{CH_2}}$) and 1.64 (quint, 2, 7.47, $\mathrm{OCOCH_2\underline{CH_2}}$).

$\underline{\mathrm{X = C_9CO_2,\ Y = COC_9}}$ 8.23 (d, 2, 8.67, ArH ortho to $\mathrm{CO_2Ar}$), 8.05 (d, 2, 8.79, ArH ortho to $\mathrm{COC_9}$), 7.31 (d, 2, 8.79, ArH ortho to OCOAr), 7.25, d, 2, 8.75, ArH ortho to $\mathrm{OCOC_9}$), 2.97 (t, 2, 7.37, $\mathrm{COCH_2}$), 2.59 (t, 2, 7.45, $\mathrm{OCOCH_2}$) and 1.77–1.72 (m, 4, $\mathrm{COCH_2\underline{CH_2}}$ and $\mathrm{OCOCH_2\underline{CH_2}}$); $\underline{\mathrm{Y = CH_2COC_8}}$ 8.23 (d, 2, 8.38, ArH ortho to $\mathrm{CO_2Ar}$), 7.27 (d, 2, 8.22, ArH ortho to $\mathrm{CH_2}$), 7.24 (d, 2, 8.26, ArH ortho to $\mathrm{OCOC_9}$), 7.17 (d, 2, 8.38, ArH ortho to OCOAr), 3.71 (s, 2, $\mathrm{ArCH_2}$), 2.60 (t, 2, 7.51, $\mathrm{OCOCH_2}$), 2.47 (t, 2, 7.33, $\mathrm{COCH_2}$) and 1.90–1.70 (m, 4,

$OCOCH_2\underline{CH_2}$ and $COCH_2\underline{CH_2}$); $\underline{Y = CH_2CH_2COC_7}$ 8.22 (d, 2, 8.67, ArH ortho to CO_2Ar), 7.24 (d, 2, 8.63, ArH ortho to CH_2), 7.22 (d overlapping 7.24, 2, ArH ortho to $OCOC_9$), 7.12 (d, 2, 8.54, ArH ortho to OCOAr), 2.92 (t, 2, 7.37, $ArCH_2$), 2.73 (t, 2, 7.37, $CH_2\underline{CH_2}CO$), 2.59 (t, 2, 7.45, $OCOCH_2$), 2.38 (t, 2, 7.33, $CO\underline{CH_2}C_6$), 1.90–1.40 (m, 4, $COCH_2\underline{CH_2}$ and $OCOCH_2\underline{CH_2}$); $\underline{Y = CO_2C_9}$ 8.24 (d, 2, 8.42, ArH ortho to CO_2Ar), 8.14 (d, 2, 8.43, ArH ortho to CO_2C_9), 7.30 (d, 2, 8.75, ArH ortho to OCOAr), 7.26 (d, 2, 8.45, ArH ortho to $OCOC_9$), 4.34 (t, 2, 6.60, CO_2CH_2), 2.61 (t, 2, 7.51, $OCOCH_2$) and 1.91–1.70 (m, 4, $CO_2CH_2\underline{CH_2}$ and $OCOCH_2\underline{CH_2}$); $\underline{Y = CH_2CO_2C_8}$ 8.22 (d, 2, 8.71, ArH ortho to CO_2Ar), 7.35 (d, 2, 8.22, ArH ortho to CH_2), 7.23 (d, 2, 8.58, ArH ortho to $OCOC_9$), 7.16 (d, 2, 8.55, ArH ortho to OCOAr), 4.09 (t, 2, 6.68, CO_2CH_2), 3.63 (s, 2, $ArCH_2$), 2.59 (t, 2, 7.47, $OCOCH_2$), 1.84–1.66 (m, 2, $CO_2CH_2\underline{CH_2}$) and 1.62–1.50 (m, 2, $OCOCH_2\underline{CH_2}$), $\underline{Y = (CH_2)_2CO_2C_7\ (GE)}$ 8.21 (d, 2, 6.79, ArH ortho to CO_2Ar), 7.25 (d, 2, 8.45, ArH ortho to CH_2), 7.22 (d, 2, 8.99, ArH ortho to $OCOC_9$), 7.12 (d, 2, 7.25, ArH ortho to OCOAr), 4.07 (t, 2, 6.52, CO_2CH_2), 2.97 (t, 2, 7.59, $ArCH_2$), 2.70–2.54 (m, 4, $OCOCH_2$ and $CH_2CO_2C_7$), 1.85–1.70 (m, 2, $CO_2CH_2\underline{CH_2}$) and 1.70–1.52 (m, 2, $OCOCH_2\underline{CH_2}$): $\underline{Y = OCOC_9}$ 8.22 (d, 2, 8.75, ArH ortho to CO_2Ar), 7.22 (d, 2, 8.55, ArH ortho to C_9CO_2), 7.19 (d, 2, 8.55, ArH ortho to OCOAr), 7.14 (d, 2, 8.87, ArH ortho to $OCOC_9$), 2.60 (t, 2, 7.21, $OCOCH_2$ acid side), 2.56 (t, 2, 7.49, $OCOCH_2$ phenol side) and 1.90–1.70 (m, 4, $OCOCH_2\underline{CH_2}$ both sides); $\underline{Y = (CH_2)_2OCOC_8}$ 8.23 (d, 2, 8.87, ArH ortho to CO_2Ar), 7.28 (d, 2, 8.43, ArH ortho to CH_2), 7.24 (d, 2, 9.87, ArH ortho to C_9CO_2, $CHCl_3$), 7.14 (d, 2, 8.54, ArH ortho to OCOAr), 4.30 (t, 2, 6.96, CH_2OCOC_8), 2.96 (t, 2, 7.06, $ArCH_2$), 2.60 (t, 2, 7.47, $OCO\underline{CH_2}C_8$), 2.29 (t, 2, 7.45, $OCOCH_2C_7$), 1.77 (quint, 2, 7.11, $OCOCH_2\underline{CH_2}C_7$) and 1.64 (quint, 2, $OCOCH_2\underline{CH_2}C_6$).

Spectra of esters with F on the acid side also gave an obvious set of two doublets for the protons ortho to CO_2Ar but not for those ortho to F. $\underline{X = F, Y = C_{10}}$ 8.22, (dd, 2, 8.90 and 5.40, ArH ortho to CO_2Ar), 7.23 (d, 2, 8.50, ArH ortho to CH_2), 7.17 (d, 2, 8.39, ArH ortho to F), 7.10 (d, 2, 8.59, ArH ortho to OCOAr) and 2.62 (t, 2, 7.69, $ArCH_2$). $\underline{Y = COC_9}$ 8.22 (dd, 2, 8.96, 5.40, ArH ortho to CO_2Ar), 8.05 (d, 2, 8.75, ArH ortho to COC_9), 7.31 (d, 2, 8.79, ArH ortho to OCOAr), 7.18 (d, 2, 8.87, ArH ortho to F), 2.97 (t, 2, 7.38, $COCH_2$) and 1.75 (quint, 2, 6.96, $COCH_2\underline{CH_2}$); $\underline{Y = CO_2C_9}$ 8.22, (dd, 2, 8.83, 5.65 ArH ortho to CO_2Ar), 8.13 (d, 2, 8.62, ArH ortho to CO_2C_9), 7.29 (d, 2, 8.71, ArH ortho to OCOAr), 7.17 (d, 2, 8.79, ArH ortho to F), 4.33 (t, 2, 6.43, CO_2CH_2) and 1.78 (quint, 2, 6.92, $CO_2CH_2\underline{CH_2}$); $\underline{Y = OC_{10}}$ 8.21, (dd, 2, 8.88 and 5.38, ArH ortho to CO_2Ar), 7.20 (d, 2, 8.58, ArH ortho to F), 7.10 (d, 2, 9.53, ArH ortho to OCOAr), 6.92 (d, 2, 9.07, ArH ortho to OC_{10}) and 3.96 (t, 2, 6.51, OCH_2); $\underline{Y = OCOC_9}$ 8.22, (dd, 2, 9.08 and 5.48, ArH ortho to CO_2Ar), 7.22 (d, 2, 9.28, ArH ortho to OCOAr), 7.19 (t, 2, 8.59, ArH ortho to F), 7.14 (d, 2, 9.32, ArH ortho to $OCOC_9$), 2.56 (t, 2, 7.45, $OCOCH_2$) and 1.76 (quint, 2, 7.28, $OCOCH_2\underline{CH_2}$.

$\underline{X = I, Y = C_{10}}$ 7.88 (s, 4, ArH ortho to CO_2Ar and I), 7.22 (d, 2, 8.47, ArH ortho to CH_2), 7.09 (d, 2, 8.58, ArH ortho to OCOAr), 2.62 (t, 2, 7.14, $ArCH_2$) and 1.58 (quint, 2, 7.25, $ArCH_2\underline{CH_2}$); $\underline{Y = COC_9}$ 8.05 (d, 2, 8.71, ArH ortho to COC_9), 8.03 (s, 4, ArH ortho to I and CO_2Ar), 7.31 (d, 2, 8.87, ArH ortho to OCOAr), 2.97 (t, 2, 7.37, $COCH_2$), 1.75 (m, 2, $COCH_2\underline{CH_2}$), $\underline{Y = CO_2C_9}$ 8.13

(d, 2, 8.46, ArH ortho to CO_2C_9), 7.90 (s, 4, ArH ortho to I and CO_2Ar), 7.29 (d, 2, 8.88, ArH ortho to OCOAr) and 4.33 (t, 2, CO_2CH_2). Y = $OCOC_9$ 7.89 (s, 4, ArH ortho to I and CO_2Ar), 7.22 (d, 2, 9.28, ArH ortho to OCOAr) and 7.14 (d, 2, 9.36, ArH ortho to OCOR), 2.56 (t, 2, 7.44, $OCOCH_2$) and 1.76 (quint, 2, J = 6.96, $OCOCH_2CH_2$).

X = C_{10}, Y = F 8.12 (d, 2, 8.27, ArH ortho to CO_2Ar), 7.34 (d, 2, 8.06, ArH ortho to C_{10}), 7.24–7.08 (m, 4, ArH ortho to OCOR and F), 2.72 (t, 2, 7.55, $ArCH_2$) and 1.78–1.50 (m, 2, $ArCH_2CH_2$); X = C_9CO 8.27 (d, 2, 8.51, ArH ortho to CO_2Ar), 8.07 (d, 2, 8.50, ArH ortho to COC_9), 7.22 (d, 2, 9.48, ArH ortho to OCOAr), 7.15 (d, 2, 8.63, ArH ortho to F), 3.02 (t, 2, 7.31, $COCH_2$), 1.80–1.73 (m, 2, $ArCOCH_2CH_2$), X = C_7O 8.13 (d, 2, 9.03, ArH ortho to CO_2Ar), 7.16 (d, 2, 9.16, ArH ortho to OCOAr), 7.17–7.11 (m, 2, ArH ortho to F), 6.97 (d, 2, 9.04, ArH ortho to OC_{10}), 4.04 (t, 2, 6.56, OCH_2) and 1.83 (t, 2, 7.0, OCH_2CH_2) and X = C_9CO_2 8.21 (d, 2, 8.79, ArH ortho to CO_2Ar), 7.24 (d, 2, 8.46, ArH ortho to $OCOC_9$), 7.12 (d, 2, 9.15, ArH ortho to OCOAr), 7.08 (d, 2, 9.16, ArH ortho to F), 2.60 (t, 2, 7.45, $OCOCH_2$) and 1.77 (quint, 2, 7.32, $OCOCH_2CH_2$).

X = CN, Y = C_{10} 8.30 (d, 2, 8.35, ArH ortho to CO_2Ar), 7.81 (d, 2, 8.10, ArH ortho to CN), 7.24 (d, 2, 7.41, ArH ortho to CH_2), 7.11 (d, 2, 8.51, ArH ortho to OCOAr) and 2.63 (t, 2, 7.59, $ArCH_2$). Y = COC_9 8.33 (d, 2, 8.75, ArH ortho to CO_2Ar), 8.08 (d, 2, 8.87, ArH ortho to COC_9), 7.85 (d, 2, 8.75, ArH ortho to CN), 7.35 (d, 2, 8.83, ArH ortho to OCOAr) and 2.99 (t, 2, 7.34, $COCH_2$). Y = CO_2C_9 8.32 (d, 2, 8.75, ArH ortho to CO_2Ar), 8.15 (d, 2, 8.99, ArH ortho to CO_2C_9), 7.84 (d, 2, 8.75, ArH ortho to CN), 7.32 (d, 2, 8.96, ArH ortho to OCOAr) and 4.33 (t, 2, 6.61, CO_2CH_2). Y = OC_{10} 8.30 (d, 2, 8.06, ArH ortho to CO_2Ar), 7.81 (d, 2, 8.06, ArH ortho to CN), 7.12 (d, 2, 8.79, ArH ortho to OCOAr), 6.94 (d, 2, 8.80, ArH ortho to OC_{10}) and 3.96 (t, 2, OCH_2). Y = $OCOC_9$ 8.30 (d, 2, 8.10, ArH ortho to CO_2Ar), 7.82 (d, 2, 8.79, ArH ortho to CN), 7.24 (d, 2, 9.16, ArH ortho to OCOAr), 7.16 (d, 2, 8.79, ArH ortho to $OCOC_9$) and 2.57 (t, 2, 7.46, $OCOCH_2$).

X = C_{10}, Y = CN 8.10 (d, 2, 8.06, ArH ortho to CO_2Ar), 7.74 (d, 2, 8.46, ArH ortho to CN), 7.36 (d, 2, 8.43, ArH ortho to OCOAr), 7.33 (d, 2, 8.14, ArH ortho to C_{10}) and 2.71 (t, 2, 7.65, $ArCH_2$); X = C_9CO 8.28 (d, 2, 8.47, ArH ortho to CO_2Ar), 8.08 (d, 2, 8.43, ArH ortho to COC_9), 7.77 (d, 2, 8.75, ArH ortho to CN), 7.39 (d, 2, 8.67, ArH ortho to OCOAr) and 3.02 (t, 2, 7.33, $COCH_2$ and X = C_9CO_2 8.23 (d, 2, 8.75, ArH ortho to CO_2Ar), 7.76 (d, 2, 8.71, ArH ortho to CN), 7.37 (d, 2, 8.79, ArH ortho to OCOAr), 7.27 (d, 2, 8.95, ArH ortho to $OCOC_9$) and 2.61 (t, 2, 7.41, $OCOCH_2$).

X = NO_2, Y = $C_{10}H_{21}$ 8.36 (s, 4, ArH ortho to NO_2 and CO_2Ar), 7.25 (d, 2, 8.69, ArH ortho to C_{10}), 7.12 (d, 2, 8.59, ArH ortho to OCOAr), 2.64 (t, 2, 7.65, $ArCH_2$), and 1.63 (t, 2, 7.78, $ArCH_2CH_2$). Y = COC_9 8.39 (s, 4, ArH ortho to NO_2 and CO_2Ar), 8.08 (d, 2, 8.67, ArH ortho to COC_9), 7.35 (d, 2, 8.79, ArH ortho to OCOAr), 2.98 (t, 2, 7.32, $COCH_2$) and 1.76 (quint, 2, 7.14, $COCH_2CH_2$); Y = CO_2C_9 8.40 (s, 4, ArH ortho to NO_2 and CO_2Ar), 8.17 (d, 2, 8.91, ArH ortho to CO_2C_9), 7.33 (d, 2, 8.71, ArH ortho to OCOAr) and 4.35 (t, 2, 6.04, CO_2CH_2), Y = OC_{10} 8.36 (s, 4, ArH ortho to NO_2 and CO_2Ar), 7.13 (d, 2, 9.16, ArH ortho to OCOAr), 6.94 (d, 2, 9.12, ArH ortho to OC_{10}) and 4.00 (t, 2, 6.76,

$ArOCH_2$) and Y = $OCOC_9$ 8.37 (s, 4, ArH ortho to NO_2 and CO_2Ar), 7.26 (d, 2, 9.20, ArH ortho to OCOAr), 7.17 (d, 2, 8.96, ArH ortho to $OCOC_9$) and 2.58 (t, 2, 7.47, $OCOCH_2$).

Elemental Analysis Calcd for $C_{33}H_{46}O_4$, X = Y = COC_9: C, 78.20; H, 9.1. Found: C, 78.02; H, 9.1.

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