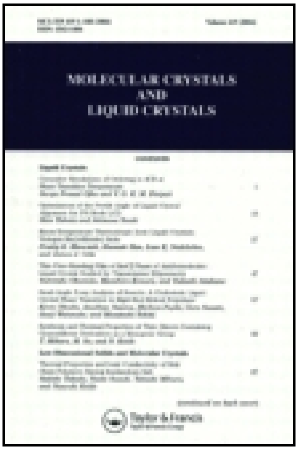


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Mesomorphic Properties of Some 4, 4′- Alkyl and Alkoxy Disubstituted Phenylbenzoates

Mary E. Neubert [a] , Michael R. Jirousek [a] & Carol A. Hanlon [a]

[a] Liquid Crystal Institute, Kent State University, 44242, Kent, Ohio

Version of record first published: 20 Apr 2011.

To cite this article: Mary E. Neubert , Michael R. Jirousek & Carol A. Hanlon (1986): Mesomorphic Properties of Some 4, 4′- Alkyl and Alkoxy Disubstituted Phenylbenzoates, Molecular Crystals and Liquid Crystals, 133:3-4, 223-233

To link to this article: http://dx.doi.org/10.1080/00268948608080814

Mol. Cryst. Liq. Cryst., 1986, Vol. 133, pp. 223–233
0026-8941/86/1334–0223/$20.00/0

Printed in the United States of America

Mesomorphic Properties of Some 4,4′-Alkyl and Alkoxy Disubstituted Phenylbenzoates

MARY E. NEUBERT, MICHAEL R. JIROUSEK,[†] and CAROL A. HANLON
Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

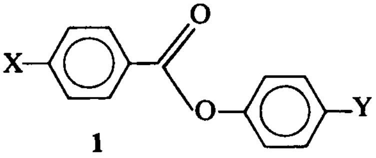
(*Received September 2, 1985*)

A variety of new 4,4′-disubstituted phenylbenzoates with one and/or both substituents as alkyl (R) or alkoxy (RO) were prepared and their mesomorphic (liquid crystalline) properties determined for later use as standards for comparison with mesomorphic properties in other new 4,4′-disubstituted phenylbenzoates. Other esters of this type, which had been previously reported, were prepared for physical studies of their mesophases and found to have different mesomorphic properties than those reported earlier. Still others were prepared to identify phases which were not determined previously. This paper presents new mesomorphic properties along with a comparison of the NMR spectra for the four possible analogs of these esters (R—R, R—OR, RO—R, RO—OR).

Keywords: phenylbenzoates, mesogens, liquid crystals, NMR

INTRODUCTION

Although the mesomorphic properties for numerous 4,4′-disubstituted phenylbenzoates **1**



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[†] Current address: Department of Chemistry, Case Western Reserve University, Cleveland, Ohio.

in which X and Y = R or RO have already been reported,[1,2] we have prepared a number of new analogs and remade some of those previously studied. Many of the new ones were prepared for use as standards in comparison studies with other new esters **1** in which X and/or Y are not R or RO. Those previously studied were remade either to identify unknown smectic phases or for use in physical studies of their mesophases. In some of these, we observed different mesomorphic properties than those reported. Thus, we would like to report our data for future reference.

MESOMORPHIC PROPERTIES

Mesomorphic properties (obtained by microscopy) for the compounds studied in this work are presented in Table I. A smectic A phase below the previously reported nematic phase was observed in the esters in which X = C_6O and Y = C_6 or C_8 and X = C_8O with Y = C_7. We also found that the phase below the nematic one in the esters with X = C_7O and Y = C_5O or C_6O was a smectic C rather than a smectic A phase as reported earlier. The textures characteristic of a smectic C below a nematic phase were observed: broken fan texture, an intermediate texture between the nematic and smectic C phase which is characteristic of only this type of phase transition, and observation of a schlieren rather than a homeotropic texture when the cover slip was moved. Additionally, this phase was miscible with the smectic C phase reported for the ester **1** with X = Y = C_8O when these two esters were mixed and no X_C-S_A transition was observed.

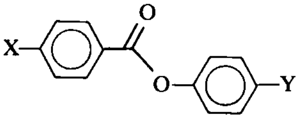
Some of the phases in the series with X = C_9O and Y = RO had not previously been identified. We found that when R = C_4, a combination of enantiotropic smectic A and nematic phases with monotropic smectic B and C phases was observed. When R ≥ C_6, the smectic B phase disappeared. This phase was identified by the observance of the characteristic transition bars between the smectic A and B phases, a focal conic fan texture similar to that observed in smectic A phases and a uniaxial cross observed in a homeotropic texture. More subtle differences were observed for other analogs as shown in Table I.

SYNTHESIS

All these esters were prepared from the corresponding 4-substituted benzoic acids and phenols using the carbodiimide method as described in Ref. 3 but with a reflux time of one rather than 4 hours. Either commercially available 4-alkoxybenzoic acids or material prepared

TABLE I

Transition temperatures (°C) for:



X	Y	C[a]	S_B	S_C	S_A	N	I
C_{10}	C_6	31.1					47.7-48.4
C_{10}	C_{10}	47.6					52.0-53.5
C_6O	C_6					45	59[b]
		22.6			(36.3-36.7)	43.0-43.7	59.6
	C_8					43	61[b]
		40.3			(42.1)	43.3-43.6	61.5-61.6
	C_9				39	39.5	66
		15.1		(25.8-26.1)	37.5-[c] 38.3	39.8-40.0	65.1-65.2
C_7O	C_5				(42)	42	61[b]
		19.8			41.1-[d] 42.3	44.4-44.8	60.4
	C_6	28.4			(45.1-45.5)	50.0-50.6	56.2-56.7
	C_8	32.6			(52.0-52.1)	52.5-54.4	60.3-60.7
	C_{10}	38.6			51.9-53.1	54.9-55.0	61.0-61.5
C_8O	C_5				56	57	66
		25			53.9-55.5	56.1-56.5	67.3-68.8
	C_6	39.4			53.3-53.5	59.2	63.0-63.1
	C_7				?	43	63[e]
		30.3			49.8-50.6	65.0-65.3	72.3-73.1
	C_8	35.0			52.0-[f] 53.4	63.8	66.2-66.3
	C_9				53.	66	69[e]
		25.2			58.0-59.3	65.7-66.1	69.2-70.1
	C_{10}	35.0			53.3-54.9	64.0-64.6	65.0-66.0
$C_{10}O$	C_7	41.1			55.4-55.8	—	70.9-71.4
	C_{10}	46.1			61.2[g]-61.9	—	74.6-75.5
	C_{12}	51.7			64.6-65.8	—	73.5-74.3
$C_{12}O$	C_{10}	65.1		(65.6-66.0)	72.9-74.2	—	75.2-75.4

TABLE I (Continued)

$C_{14}O$	C_7	49.6	(59.5–59.7)	—	69.0–69.6	—	75.3–76.3
	C_8	58.2	—	(64.2–64.5)	69.9–70.3	—	74.3–76.6
	C_{10}	70.5	—	(73.4–73.7)	(76.3–77.7)	—	79.0–79.2
C_7O	OC_5				(~50)	58	81.5[h]
		42.7		(47.6)	—	58.8–59.2	82.1
	OC_6				(51)	67	87[h]
		42.4		(51.4)	—	65.5–65.9	86.7
C_8O	OC_8			62.5	—	73.5	90.5[b]
		49		60.9–61.4	—	72.0–72.1	92.3–92.5
C_9O	OC_4				61.7[i]	73.3	87.5[b]
		32	(50.3)	(61.5–61.6)	62.2	72.0	86.7
	OC_6			66.1[i]	—	74.9	88.2[b]
		41.9		63.7–65.8	73.6	74.1–74.8	88.2
	OC_8			67.2[i]	—	80.5	90.1[b]
		58.3		66.1–66.9	—	79.2–79.3	89.1–89.3
	OC_{10}	57.7		69.9–72.3	—	82.8–82.9	88.8–88.9
$C_{10}O$	OC_5		(46)[i]	63.5	68	80.5	85.5[h]
		39.4	(45.3–45.8)	61.5–62.6	66.7–67.1	79.3–79.4	84.5–84.8
	OC_6		(44.5)[i]	62.5	77.5	83.5	89.5[h]
		41.0	(42.8–43.6)	60.1–61.2	76.4–76.7	82.4	88.3–88.5
	OC_{10}	32.0	—	40.4–42.3	—	42.3–42.5	56.2–56.3
$C_{11}O$	OC_5		(51)[i]	64.5	67	85	87[j]
		48.0	(49.6–49.8)	(67.1–67.3)	70.7–72.3	82.0–82.7	83.1–83.7
	OC_6		(54)[i]	61	79.5	86.5	88[k]
		40.4	(49.3–49.7)	68.4–69.2	78.5	84.8–85.0	87.0–87.3
$C_{12}O$	OC_{10}	63	—	81.0–81.3	—	—	91.9–92.0
$C_{14}O$	OC_7	56.2	60.1–61.0	67.0–67.2	84.7–85.2	—	89.0–89.2

[a] Crystallization temperature obtained on cooling at 2°/min.

[b] Data from Ref. 1a.

[c] This phase was of such a short range that it was often difficult to detect on heating.

[d] A crystal-crystal change was observed on heating at 36.7–37.7°.

[e] Data taken from Ref. 2.

[f] A crystal-crystal change was observed on heating at 46.2–47.4°.

[g] A crystal-crystal change was observed on heating at 58.4–60.0°.

[h] Data from Ref. 1b.

[i] This phase was not identified in the literature.

[j] Data taken from Ref. 1c.

[k] Data taken from Ref. 1d.

using the procedure described in Ref. 4 was used. 4-Decylbenzoic acid was prepared using the method described in Refs. 5 and 6 and 4-alkoxyphenols were prepared using the procedure described in Ref. 4. We found that commercially available 4-alkylphenols were contaminated with small amounts of ortho and meta isomers preventing adequate purification of the esters prepared from these by recrystallization. Therefore, we used only material prepared using the method described in Ref. 7. All these esters were recrystallized three times from abs EtOH and showed one spot on TLC ($CHCl_3$, Anal Tech Silica gel, UV).

CHARACTERIZATION

Microscope studies were done using either a Leitz-Ortholux or Laborlux 12 POL polarizing microscope fitted with a modified Mettler FP-2 heating stage with a heating or cooling rate of 2°/min. More details of our method are provided in Ref. 8 and typical examples of textures given in Ref. 9.

The esters were identified by a characteristic IR absorption at 1740 cm^{-1} for aromatic ester carbonyl groups. NMR data (in CCl_4 with TMS as a standard using a Varian EM-360 instrument) were obtained for all esters to determine purity and to substantiate their structures. These data make it possible to compare NMR characteristics for the four possible analogs (R—R, R—OR, RO—R, and RO—OR) as presented in Figure 1. The aromatic protons ortho to the ester carbonyl group (H_b) appeared as a doublet at δ ~8 ppm for all these esters. In three of them, the protons ortho to the ester ether (H_c) occurred as a doublet at δ ~7.1 to 7.2 ppm (Figures 1a, b, and d). However, in the RO—R series (Figure 1c), these occurred as a singlet overlapping with the singlet from the protons ortho to the alkyl group on the phenolic end, H_d. In the series with no alkoxy groups i.e. R—R, the protons ortho to both alkyl groups (H_a and H_d) appeared as a singlet at δ ~7.0 ppm establishing the chemical shift for these protons (Figure 1a). When the ester has an acid alkyl and a phenolic alkoxy substituent i.e. R—OR, the protons ortho to the alkyl group (H_a) occur as a doublet (δ ~6.94 ppm) overlapping with the doublet for the protons ortho to the alkoxy group (H_d) at δ ~6.81 ppm (Figure 1b). Since there are only slight variations in the chemical shifts for these three proton types, spin decoupling experiments were done on the (R—OR) and (RO—R) compounds. H_b was irradiated in order to collapse the H_c doublet to a singlet. This made it possible to make definite assignments for these three protons and establish the relationship between the chemical shifts for the protons ortho to these

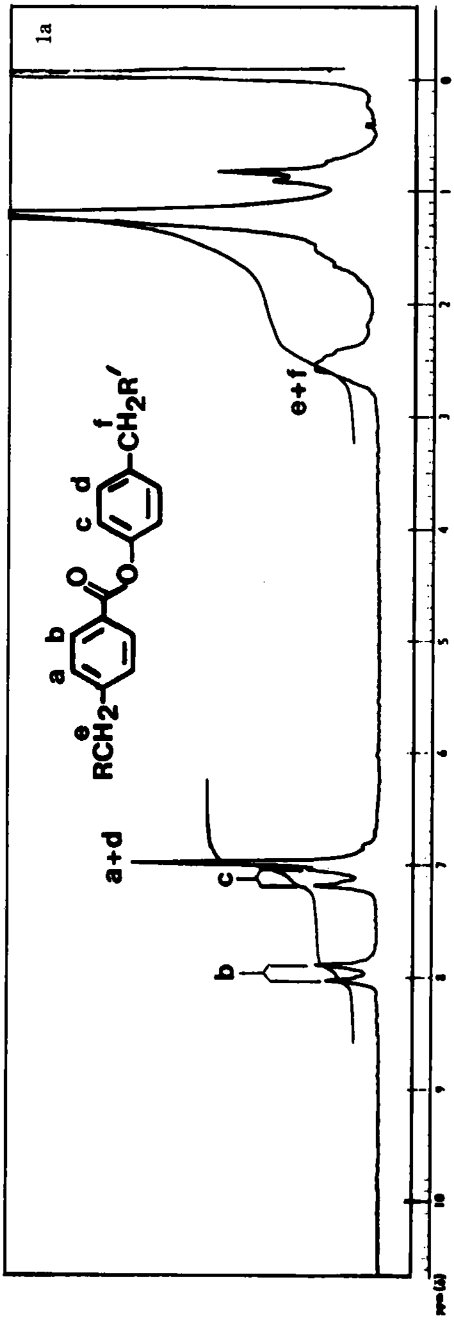


FIGURE 1A A comparison of NMR spectra for 4,4′-disubstituted phenylbenzoates.

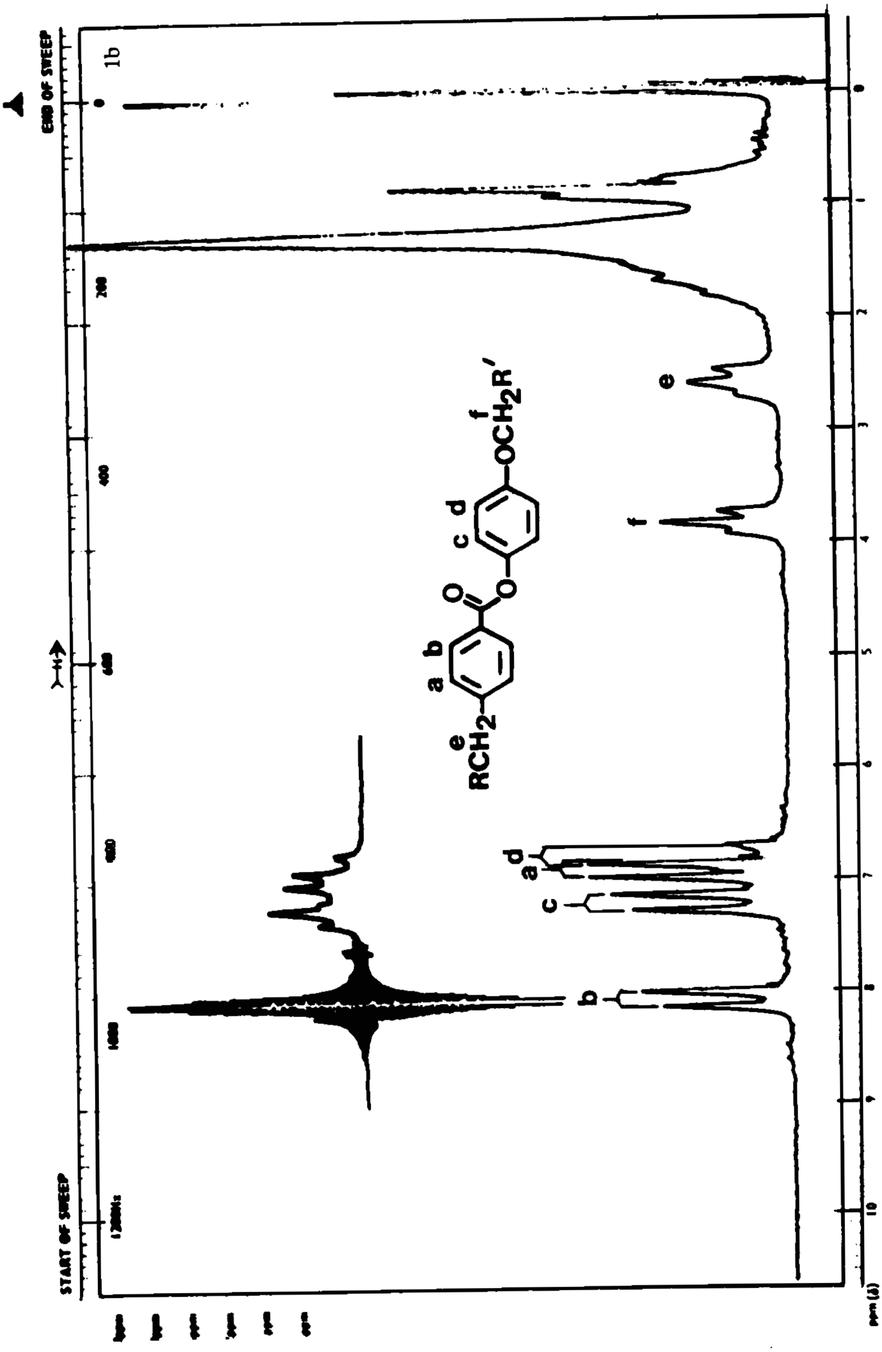

1b
END OF SWEEP
START OF SWEEP
200
400
600
a
b
c
d
e
f
RCH_2
O
OCH_2R'
0
1
2
3
4
5
6
7
8
9
10
ppm (δ)

FIGURE 1B

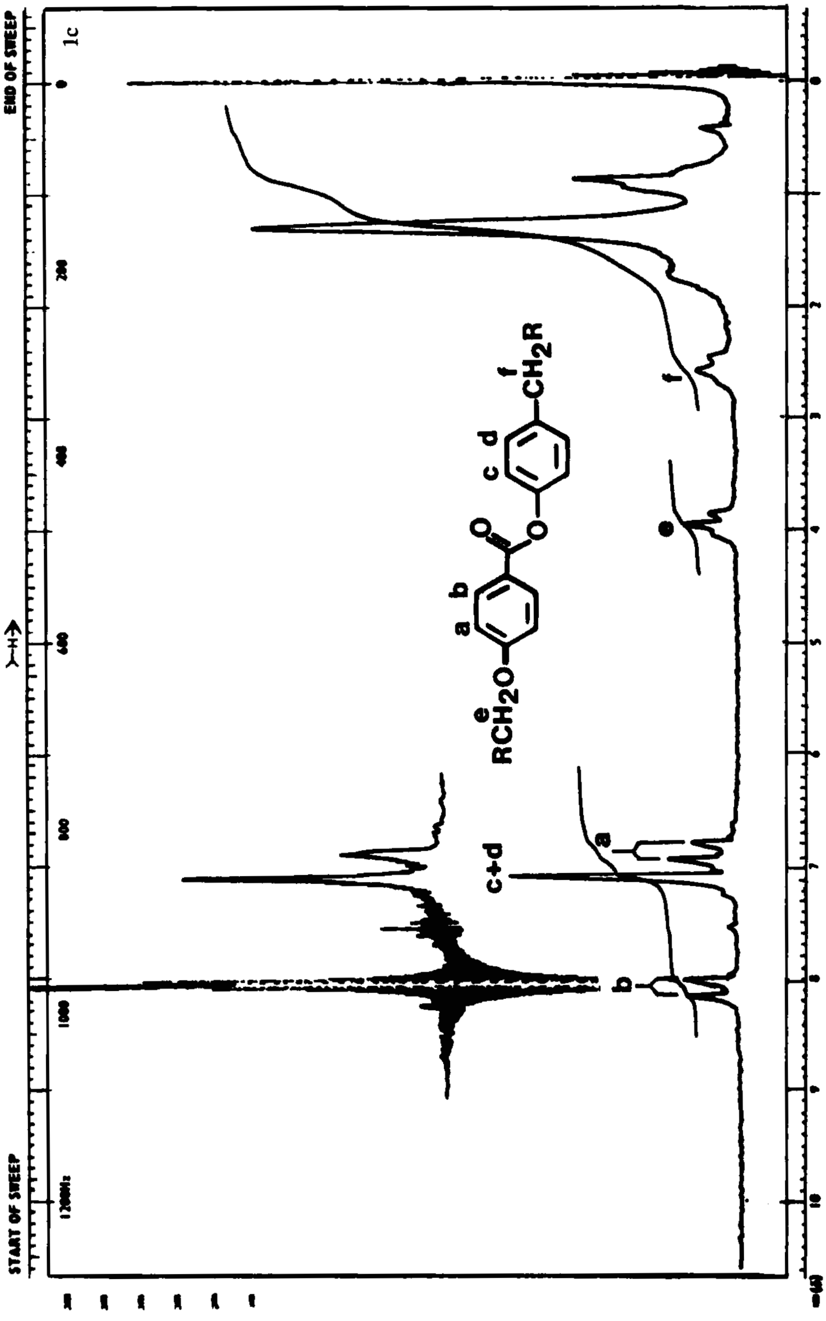

1c
END OF SWEEP
START OF SWEEP
1200Hz
0
200
400
600
800
1000
a
b
c+d
e
f
a b
c d
e
RCH2O
O
f
CH2R
0
1
2
3
4
5
6
7
8
9
10

FIGURE 1C

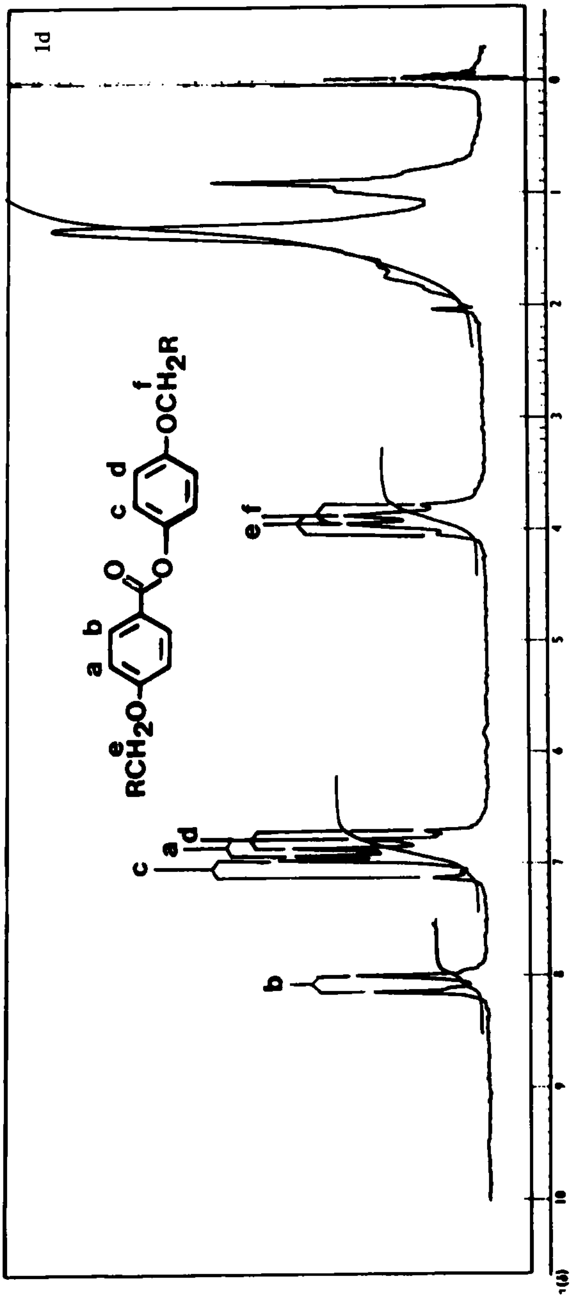
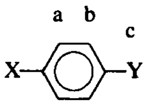


FIGURE 1D

TABLE II

NMR Chemical shifts for



Chemical shift (δ)

X	Y	a	b	c	α-CH_2 in R
R	CO_2H	7.13	7.99	—	2.5
RO	CO_2H	6.90	8.05	9.54	4.0
R	OH	6.90	6.58	5.58	2.48
RO	OH	6.78	6.78	5.43	3.90

three substituents. The presence of two alkoxy substituents gave a set of three overlapping doublets with increasing chemical shift in the order of protons ortho to OCO > RO on the acid > RO on the phenol (Figure 1d). The overlapping of the peaks for the protons H_c and H_d in the RO—R series leaves a singlet at δ = 6.85 ppm for the protons ortho to the alkyl group (H_a) (Figure 1c). All the aromatic coupling constants were ~9 Hz.

In the dialkyl esters, the α-methylene protons appeared as a broad peak at δ ~2.58 ppm (Figure 1a) but in the dialkoxy esters, two overlapping triplets with J ~ 6Hz occurred at δ ~3.99 (H_e) and 3.89 (H_f) (Figure 1d). Two triplets were also observed in the two series containing both alkyl and alkoxy groups as one would expect. The protons ortho to the alkyl group occurred at δ ~2.6 whether on the acid (H_c, Figure 1b) or the phenolic end (H_f, Figure 1c) whereas those ortho to the alkoxy group occurred at slightly different chemical shifts depending on whether they were on the acid end at δ ~3.95 (H_e, Figure 1c) or the phenolic end at δ ~3.86 (H_f, Figure 1b) in agreement with what was observed for the dialkyl and dialkoxy series. The coupling constant for the triplet ortho to an alkyl group was a little larger (~7Hz) than that observed for the triplet ortho to the alkoxy group (~6Hz).

NMR data for the aromatic protons for the starting phenols and acids (see Table II) were also useful in making these assignments.† A set of two doublets with J ~ 9Hz was observed for the aromatic

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† NMR assignments were incorrectly made for the aromatic protons in the 4-alkylphenols and thiols in Ref. 7. The correct assignments are presented in Table I.

protons in all these compounds except in the 4-alkoxyphenols which showed only a singlet. The α-methylene protons always occurred as a triplet with a slightly larger coupling constant when in an alkyl chain ($J \sim$ 7Hz) than in an alkoxy one ($J \sim$ 6Hz). When these protons were part of an alkyl chain, the chemical shift was the same whether the chain was ortho to an OH or a CO_2H but differed slightly when they were in an alkoxy chain. Like most acidic protons on oxygen atoms, the hydroxy and carboxylic acid protons were not always observed but appeared as either broad or sharp singlets when they were.

Acknowledgments

The partial financial support of the National Science Foundation in the form of grant number DMR83-09739 is greatly appreciated. We would also like to thank the Chemistry Department for use of their Varian EM-360 NMR instrument, and the following people for preparing some of these esters: Roger Beitzel, Frank Herlinger, Stan Laskos, Jr, Katherine Leung, Thomas Santora, Martha Stahl, Mark White, and Patricia Wildman.

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