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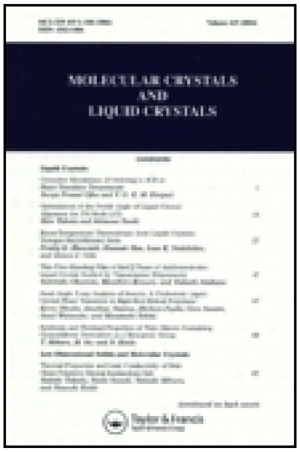

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The Effect of Carbonyl Containing Groups in the Terminal Chains on Mesomorphic Properties in Aromatic Esters and Thioesters. l. α-keto Groups on the Phenolic End

Mary E. Neubert [a] , Frank C. Herlinger [a] , Michael R. Jirouskek [a] & Adriaan De Vries [b] [a]
[a] Liquid Crystal Institute, Kent State University, Kent, Ohio, 44242
[b] Department of Chemistry, Case Western Reserve University, Cleveland, Ohio

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The Effect of Carbonyl Containing Groups in the Terminal Chains on Mesomorphic Properties in Aromatic Esters and Thioesters. I. α-Keto Groups on the Phenolic End

MARY E. NEUBERT, FRANK C. HERLINGER, MICHAEL R. JIROUSEK,† and ADRIAAN DE VRIES

Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

(*Received February 3, 1986*)

The effect of inserting a ketone group in the α-position of the alkyl chain on the phenolic end of 4,4′-disubstituted phenylbenzoates and di-(4′-substituted phenyl)-*trans*-cyclohexane-1,4-dicarboxylates on mesomorphic properties as compared to those properties observed for the corresponding alkyl compounds was determined. Transition temperatures were higher and mesophase ranges usually wider in the α-keto compounds in both series. Nematic phases were observed in both series, but a strong preference for a single smectic phase predominated with this being a smectic A phase in the phenylbenzoates and a smectic C phase in the cyclohexane diesters. A variety of crystal changes and a few complex melting transitions were also observed in the cyclohexane diesters.

Keywords: liquid crystals, x-ray, phenylbenzoates, phase transistors, trans-cyclohexane-1,4-dicarboxylates

INTRODUCTION

The mesomorphic properties of many organic compounds have been determined in attempts to discover relationships between molecular structural features and mesomorphic properties. Some relatively gen-

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

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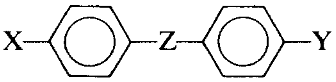
eral trends have been observed for those structural features which favor any mesomorphic properties and nematic versus smectic phases. Less definite relationships are known for specific types of smectic phases or phase sequences. Such relationships would be useful in designing new mesogens which would have the types of phases or phase sequences desired by researchers studying the physical properties of smectic phases or those phases of interest for use in displays with a variety of applications. Three aspects of mesomorphic properties are of interest in studying these relationships:

1. Transition temperatures,
2. types of mesophases, and
3. ranges of the mesophases.

Numerous variations of the central group Z of the most popular structure **1**



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have been synthesized and the mesomorphic properties determined. Some general trends have been observed which are useful in designing new mesogens. Extensive studies have been done on the effect of the central group Z on mesomorphic properties. However, changing Z involves a large structural change and changes several structural features at one time. Changing Z, for example, affects the total three-dimensional structure by changing its planarity. This affects the packing of the molecules which is known to influence the types of mesophases which are observed.

The effect of various terminal substituents, X and Y, on mesomorphic properties has also been studied extensively. Much of this work has been concerned with studying the effect of various chain length alkyl containing substituents i.e., homologous series. From these studies, we know that nematic phases are more likely to occur and predominate at shorter chain lengths and smectic phases at longer ones with the loss of mesomorphic properties when the chain becomes too long. Since the addition of more methylene groups does not affect the three-dimensional structure of the molecule as does the central group, the changes in the types of smectic phases observed are generally not as large as with the central group.

The effect of placing a functional group between the benzene ring

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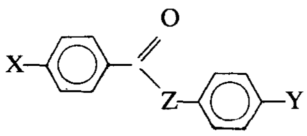
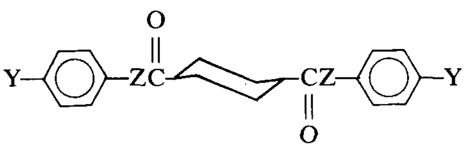
and the alkyl chain has also been studied, particularly the insertion of an ether oxygen atom. However, when the oxygen atom is attached directly to the ring it can be considered either as part of the rigid core of the molecule due to resonance between the oxygen *p* electron pair and the aromatic π electrons or as part of the flexible tail. Thus, substituting an alkoxy for an alkyl substituent involves modifying both the core and the tail in these molecules. Additionally, it has been shown that steric hinderance can occur between substituents on the α-carbon of the alkyl chain and the aromatic protons ortho to this chain and greatly affect the mesomorphic properties observed.[1,2]

We felt that if a functional group were inserted into the terminal chain in a position that was not adjacent to the benzene ring, the relationships between molecular structure and mesophases might be simplified since large changes in the three-dimensional structure of the molecules would not occur. If this were true, it might be possible to fine-tune the mesomorphic properties of a compound by using these modifications to retain the smectic phases determined by the central group but increase their ranges or lower the temperatures at which they occur. Additionally, since the type of terminal chain does have some effect on the type of smectic phases observed, we hoped to learn more about the relationship between molecular structure and the types of smectic phases observed. Of course, new mesogens would be synthesized as well and hopefully, some of these would have phases of interest in studies of the physical properties of mesogens or in designing new displays.

To accomplish this, a systematic study of the effect of terminal functional groups in various positions along the chain on mesomorphic properties was needed. This required that two major decisions be made: 1) which basic core structure should be used and 2) the terminal functional group that would be studied. Two ester series **2** and **3**



2a Z=O, **b** Z=S



3a Z=O, **b** Z=S

were chosen for a variety of reasons. We felt it was necessary to study the effect of the same terminal chain on two largely different structures since it is known that mesomorphic trends observed in one series are not always observed in other series. The phenylbenzoates

2a (X and Y=R or RO) have been extensively studied both by ourselves[1,2] and others[3] so that many of the standards we would need in this series for comparisons of mesomorphic properties have already been studied eliminating the need to prepare many of these compounds. Data for many of the thioesters **2b** and the cyclohexane diesters **3a** in which X and Y=R and/or RO are also available[4–6] leaving only the cyclohexane dithioesters **3b** which would have to be prepared as standards. These data indicate that the phenylbenzoates **2a** have transition temperatures below 100° but relatively short range mesophases whereas the diesters **3a** have higher temperatures but wider mesophase ranges. Thus, these two series would be ideal to determine if it will be possible to fine-tune the mesomorphic properties of these compounds to give longer phase ranges at lower temperatures.†

Obviously, many compounds would be needed to do a good systematic study. Since the esters **2** are prepared by the reaction between two major starting materials, the 4-substituted acids and phenols or thiols (the latter could also be used to prepare the cyclohexane diesters **3**), these esters are among the easiest core structures to synthesize and modify. Once the acids and phenols are prepared, they could be combined in an infinite number of possibilities. The need to proceed through a multistep synthesis every time a chain modification is needed on either side of the molecule, as is true in the biphenyl series, can be avoided in these esters. The bulk of the synthesis work would be in the preparation of the intermediates and not in the mesogens. These esters have the advantage of being chemically stable as well.

A variety of factors also influenced our choice of which terminal functional group should be studied. Two types of such groups are known to organic chemists: those which are univalent and those which are divalent. Only divalent groups could be inserted between the chain and the benzene ring or between two segments of the tail. Monovalent groups could only be attached to various carbon atoms along the chain. Although these groups could lead to interesting structural-mesomorphic property relationships, these would be complicated by factors such as steric hindrance to packing between molecules. Carbonyl containing groups, all of which are divalent, provide a variety of modifications which could be inserted between

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†The idea that this could also be accomplished by mixing a phenylbenzoate **2** with a cyclohexanediester **3** is not supported by our recent studies on mixtures of these and similar compounds which indicates that in such mixtures large range induced nematic phases are formed with elimination of many of the smectic phases (see Reference 7).

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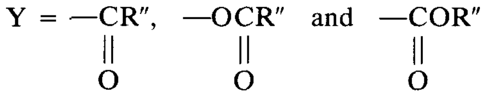
chain segments and also be synthetically feasible. Thus, we chose to begin our studies with

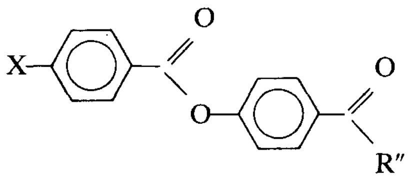


$$Y = -\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{R''},\quad -\mathrm{O}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{R''}\quad \text{and}\quad -\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{OR''}$$

with R″ = a straight chain alkyl group since these were the simplest to prepare and would provide the necessary standards and then move these groups out along the chain away from the benzene ring on the phenolic end of **2a** and **3a**. Since we had found earlier that a chain modification on the acid end of the phenylbenzoates **2a** has a larger effect on their mesomorphic properties than the one on the phenolic end,[2] it will also be necessary to study the same modifications on the acid end since this could lead to another way of fine-tuning the mesomorphic properties in these series. However, many of the required acid intermediates are more difficult to prepare than the analogous phenols so that results in this area will take longer to obtain.

Initially, a large number of homologs and in one instance (Y = OCOR″) a homologous series was prepared to determine the trends of mesomorphic properties in each series. However, it soon became apparent that this was unnecessary and that usually only two or three homologs properly chosen would be enough to determine these trends. Therefore, the C_{10} chain length (the total number of carbon atoms) both for X and Y was usually chosen as the first one to be prepared with C_8 and C_{12} often being added to more accurately determine the trends that would occur in a series. If the trends could not be definitely established with these homologs or the mesomorphic properties were particularly interesting, more homologs were prepared. At times, it was necessary to prepare the corresponding R/RO esters since data were not always available for a particular homolog used in a comparison. Much of the new data for these esters have already been reported in Reference 8.

In this first paper in this series, we present the mesomorphic properties observed for the α-keto esters **4**



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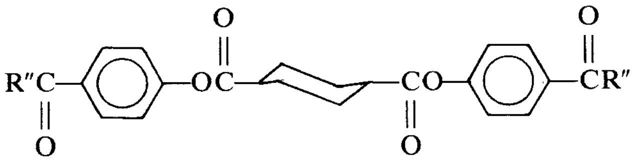
in which X = R or RO and the corresponding diesters **5**



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Mesomorphic properties for some α-keto phenylbenzoates have already been reported,[9,10] but these all contained a short R″ group which is generally more favorable for observing nematic than smectic phases.

MESOMORPHIC PROPERTIES

Transition temperatures for the α-keto phenylbenzoates **4** synthesized in this work are presented in Table I. Only smectic A phases were observed but nematic phases have been reported in some of the shorter chain R″ compounds.[9,10] A comparison of the melting and clearing temperatures for these esters with X = RO with those for the corresponding alkyl esters **2a** (X = RO, Y = R′) presented in Table II shows an increase of ~27–68° in both these temperatures for most of the α-keto esters. Within a homologous series the clearing temperatures remained fairly constant when R > C_4 while the melting points showed a gradual rising trend (Figure 1).

When the mesomorphic properties of these two series were compared using the same number of carbon atoms in the R′ group as the total number found in Y = COR″† as shown in Figures 2 and 3, a definite trend of enhancement of the smectic A phase at the expense of the nematic phase was observed. This is also true when X = R (which also have higher transition temperatures than when Y = R′) with the S_A phase being preferred over a S_B phase at longer R chain lengths (Figure 4). In both the α-keto series, the nematic phase is quickly lost at short R″ chain lengths. Although the phase length of the S_A phase decreases at longer R″ lengths after an initial increase, it appears that it will persist for a while with R″ > C_9 (see Figure 1).

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†Data were not always available for the exact chain lengths but were for adjacent ones. Much of this data comes from Ref. 3. No crystallization temperatures were available for these compounds.

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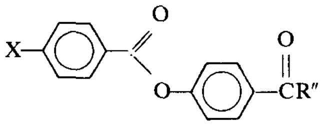
TABLE I

Transition temperatures (°C) for



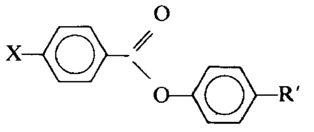
X	R″	C[a]	S_A	I
C_6	C_5	82.3	(80.4)[b,c]	90.2–91.6
	C_7	81.0	(85.5–85.8)[b]	90.5–91.4
C_9	C_5	76.6	86.4–86.7	88.2–88.5
C_{10}	C_4	70.4	81.4	86.3–87.3
	C_5	86.8	87.8	92.9–93.3
	C_7	88.9	(92.8–93.0)[b]	96.3–97.1
	C_9	95.0[d]	—	101.6–101.8
C_5O	C_5	77.3[e]	90.5	111.3–111.5
C_6O	C_7	78.2[f]	93.9–94.9	119.3–119.5
C_7O	C_5	78.3	97.0–97.3	117.4–117.8
	C_7	89.5	101.9–102.6	119.4–119.6
C_8O	C_5	87.8	99.8–100.3	119.2–119.6
	C_7	86.8	98.7–99.7	120.7–121.3
$C_{10}O$	C_4	77.8	91.2–92.6	120.4–120.6
	C_7	92.5	105.0–105.5	121.1–121.2
	C_9	95.8	107.0–107.6	120.4–120.7
$C_{12}O$	C_4	80.3	96.2–96.6	120.5–120.8
	C_7	102.9	106.9–107.6	119.4–119.5
	C_9	104.2	109.7–112	119.1

[a] Crystallization temperature obtained at a cooling rate of 2°/min.
[b] ( ) indicates a monotropic transition.
[c] Crystals began to grow slowly before the S_A phase was observed.
[d] A crystal-to-crystal change on heating was observed at 92.0–95.0.
[e] Crystal-to-crystal transition at 86.8–88.2.
[f] Crystal-to-crystal transition at 85.2–87.4.

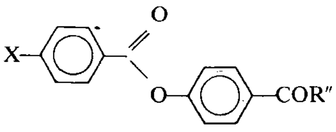
This trend towards S_A phases in the α-keto phenylbenzoates was, however, not observed in the cyclohexane diesters. Instead the transition temperatures for this series presented in Table III show only N and S_C phases. Initially only the longer R″ chains were prepared but to be certain no S_A phases were lost in these longer lengths, some shorter homologs were also prepared. No S_A phases or S_A–S_C combinations were observed. Long range nematic phases were seen with $R'' < C_5$ (Figure 5). At $R'' = C_5$, the smectic C phase is introduced and grows rapidly in its range until the nematic phase is eliminated to give a very long range S_C phase of 93° when $R'' = C_9$. Obviously, this S_C phase will persist at even longer R″ lengths. A comparison of the mesomorphic properties of the α-keto series (Figure 5) with those

TABLE II

Comparison of the melting and clearing transition temperatures for:



versus



X	R′	R″	Difference (°C)	
			mp	Clp
C_6O	C_2[a]	C_1[b]	0	27
	C_3[a]	C_2	33	64.4
	C_4[a]	C_3[b]	39.9	52.3
	C_8[a]	C_7	51.9	54.5
C_8O	C_6	C_5	47	67.7
$C_{10}O$	C_5[a]	C_4	50.5	53.1
	C_{10}	C_9	45.7	45.2
$C_{12}O$	C_{10}	C_9	38.3	42.9

[a] Data in Ref. 3a.

[b] Data in Ref. 3c.

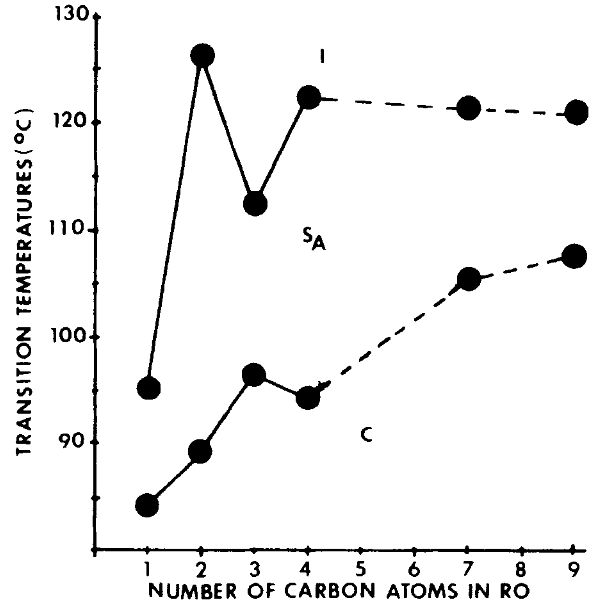
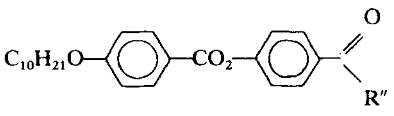


FIGURE 1 Transition temperatures (°C) versus alkyl chain length for



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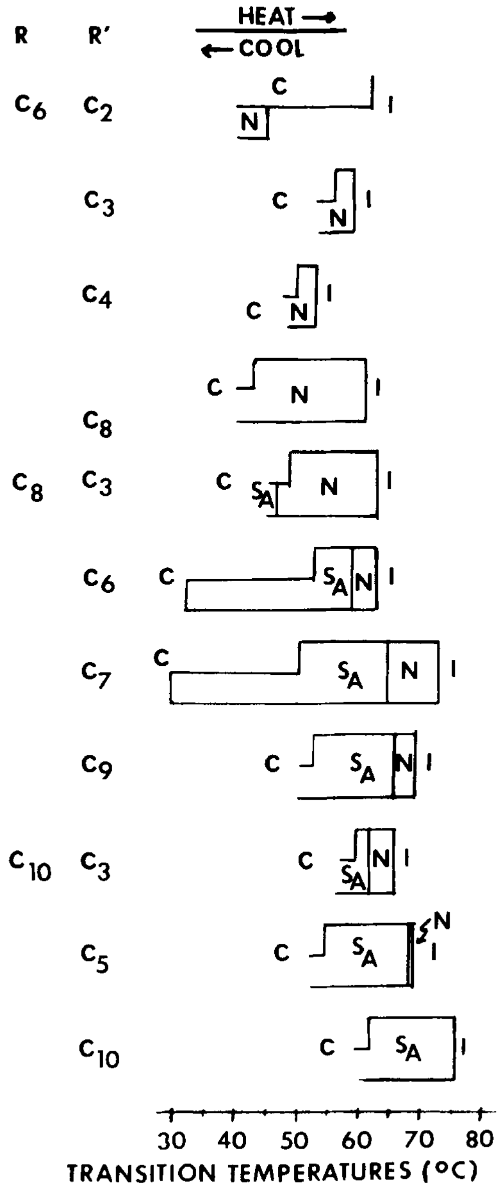
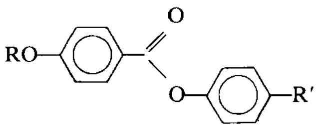


FIGURE 2 Mesomorphic properties for



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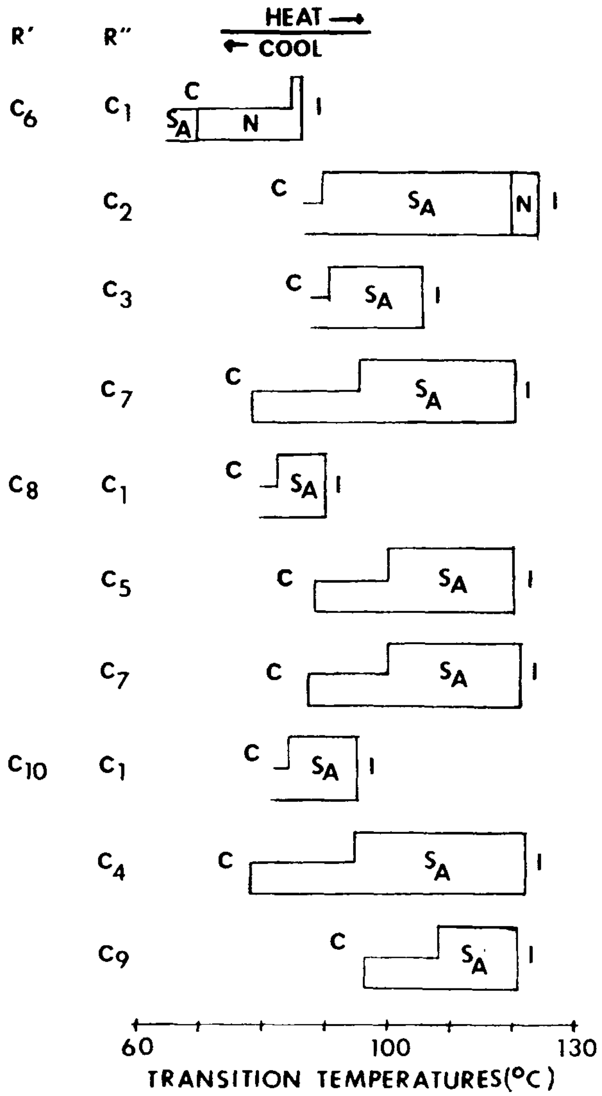
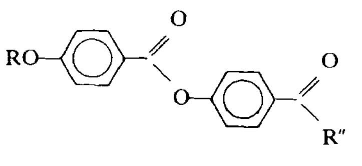


FIGURE 3 Mesomorphic properties for



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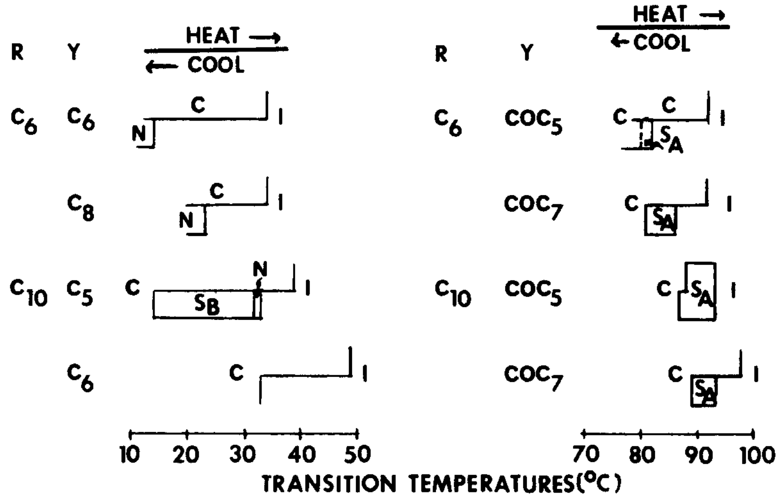


FIGURE 4 Mesomorphic properties for

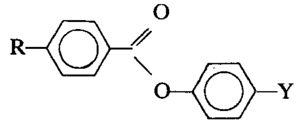
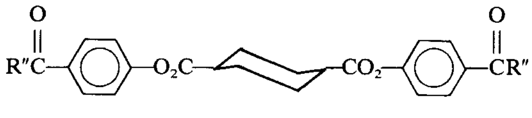


TABLE III

Transition temperatures (°C) for



R″	C[a]	S_C	N	I
C_2	133.5	—	183.5–185.3	239.3–240.8
C_3	132.7[b]	—	137.3–141.9[c]	219.4–219.5
	122.2[b]	—	157.2–158.5[c]	
C_4	131.3	—	139.9–144.0	201.3–201.5
C_5	89.4[b]		143.3–145.4[c]	197.7–198.7
	104.5[b]	107.6–108.6	120.1–123.3[c]	
C_7	94.1[b]	107.0–108.7	177.7–178.8	192.7–192.9
C_9	95.6	103.4–104.5	—	186.7–189.2

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

[b] Crystal-crystal changes were observed in this compound. Details are given in the mesomorphic properties section.

[c] Two melting points were observed in this homolog. More details are presented in the mesomorphic properties section.

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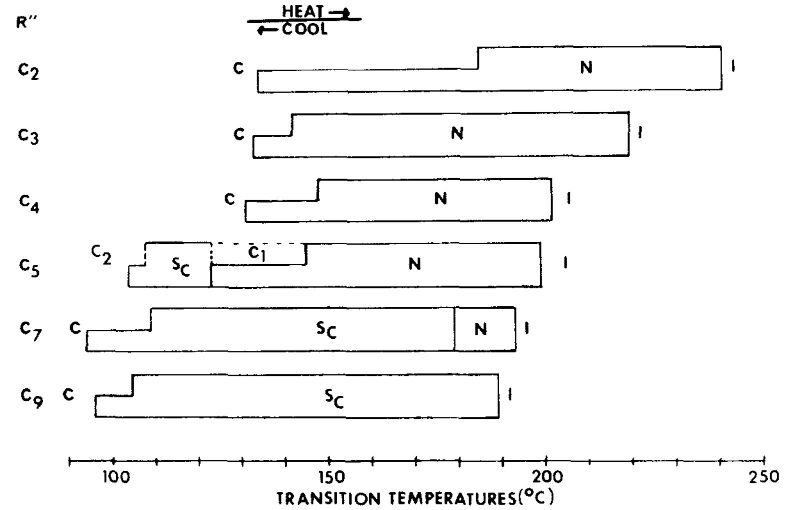
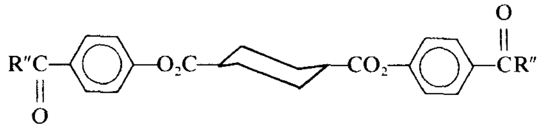


FIGURE 5 Mesomorphic properties for



for the alkyl series (Figure 6, data are from Ref. 6) shows a replacement of the uniaxial S_A and S_B phases observed in the alkyl series with the tilted S_C phase in the α-keto series. Transition temperatures were also found to be higher in the α-keto series by a magnitude similar to that observed in the phenylbenzoates (Table IV). In both series, this increase was often larger for the clearing than the melting points. Fewer mesophases were observed in the α-keto than in the alkyl series, but the total enantiotropic mesophase ranges were generally larger for both α-keto series. Thus, each mesophase observed had a wider range than those found in the corresponding alkyl esters. In the α-keto phenylbenzoates, smectic A phases were observed whether X was R or RO, unlike the corresponding alkyl series, but the ranges were considerably shorter when X = R, as is also true with the dialkylphenylbenzoates.

Microscopic observations of the smectic C phase in the C_5 cyclohexane homolog **5** (R'' = C_5) on cooling showed large and continuous textural changes until crystallization occurred much like that observed in the textures of smectic C phases with temperature dependent tilt angles that occur below a smectic A phase. Therefore, the nematic-to-smectic C transition was studied very carefully in search of an

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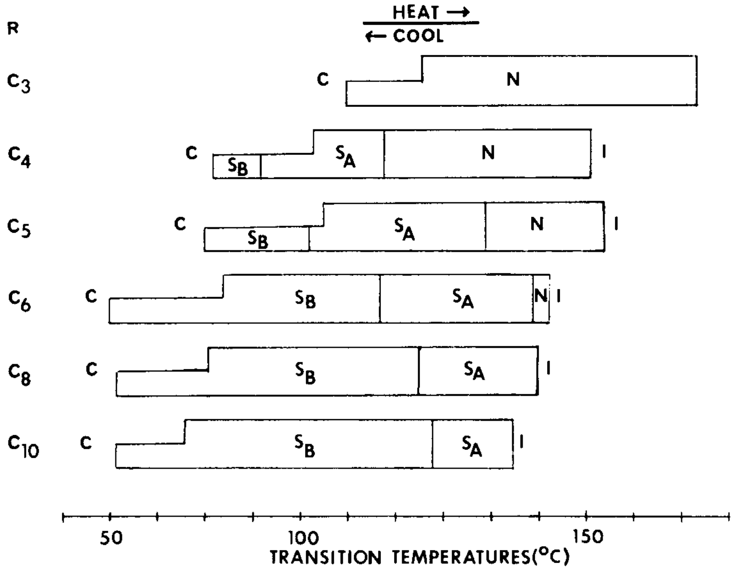
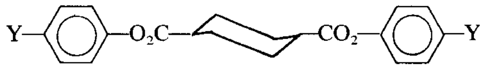


FIGURE 6 Mesomorphic properties for

TABLE IV

Comparison of the melting and clearing temperatures for:



Y = R′ and R″CO

R′[a]	R″	Difference (°) mp	Difference (°) Clp
C_3	C_2	69.3	67.3
C_4	C_3	49.3, 65.9[b]	68.5
C_5	C_4	34.0, 48.7[b]	47.9
C_6	C_5	70.9	57.4
C_8	C_7	37.9	53.3
C_{10}	C_9	38.8	54

[a] Data from Ref. 6.

[b] Two melting points were observed for this keto compound. See Table III.

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indication that a short-range smectic A phase was present. A colored marbled nematic texture was observed carefully on cooling but showed only the schlieren and broken fan textures growing simultaneously and no homeotropic texture which would indicate the presence of a smectic A phase. Smaller changes were observed on cooling the smectic C phase in both the C_7 homolog which has a nematic phase and the C_9 homolog which does not. These continuous changes stopped long before crystallization occurred in these much wider range smectic C phases. Tilt angles with a small temperature dependence have been observed in some compounds having smectic C phases below nematic and isotropic liquids[11,12] but a tilt angle with a large temperature dependence like those observed in some S_C–S_A transitions[11,13] appear to have been reported only rarely for such cases (e.g., Figure 5 in Ref. 25). Layer spacings in the S_C phase were determined from x-ray diffraction studies for the C_5 and C_7 homologs. For both compounds, the change in the layer spacing as a function of temperature is only very small, of the order of 1%. It should be kept in mind, however, (1) that in a number of smectic C phases below A phases the observed changes in the layer spacing have also been very small, e.g., only 0.7% in the C_8 homolog of series **3a** ($Y = C_8O$),[14a,b] and (2) that even if the layer thickness remained constant it would still be possible for the angle between the director and the layer normal to change significantly.[14a,c] More detailed x-ray data will be presented in a later paper.

A variety of crystal changes were observed in many of these compounds. In some homologs, two melting points were observed as well. When $R'' = C_3$, crystals formed on cooling the nematic phase to 132.7° (C_1). When these crystals were reheated without further cooling, they melted to the nematic phase at 137.3–141.9° ($C_1 \rightarrow N$). Fresh crystals also melted at this temperature. However, if the crystals were cooled further, a crystal change occurred at 122.2° (C_1–C_2). When these were heated, they melted to the nematic phase at 157.2–158.5° ($C_2 \rightarrow N$). That these were crystalline rather than liquid crystalline phases was shown by variations in the temperatures at which they formed on cooling as well as supercooling and their typical crystalline textures. When $R'' = C_4$, the fresh crystals seemed to undergo a crystal change on heating at 99.1°. Cooling the nematic phase to 99.0° gave a highly colored mosaic texture which immediately and rapidly changed to a feathery crystalline texture. When these crystals were heated, they melted at ~144°. Two different crystalline forms were observed when $R'' = C_5$. Fresh crystals (C_1) melted to

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the nematic phase at 141.2–145.5° ($C_1 \rightarrow N$). Cooling this phase gave a smectic C phase which when cooled to 101.9° gave mosaic crystals (C_2). Reheating gave the smectic C phase at 107.6–108.6° ($C_2 \rightarrow S_C$). However, when these crystals were cooled further before reheating, a crystal change (feathers) was observed at 89.5°. These crystals melted directly to the nematic phase on heating to 141.3–145.4° and therefore are thought to be the same as the fresh crystals C_1. If the smectic phase was cooled rapidly to the crystalline state, a wide range melting point was observed indicating a mixture of crystalline forms. Crystallizations occurred rapidly when cooling was done at 2°/min and textures looked like crystals with sharp edges on the growing front in the mosaic texture (C_2) in this homolog. Both crystalline phases, C_1 and C_2, were also observed in our x-ray studies, but no detailed analysis of the C_2 phase was possible because the C_2 phase quickly converted to the C_1 phase. When $R'' = C_7$, crystallization occurred at 94.1° (C_1) on cooling the smectic C phase. A crystal change was observed on further cooling at 92.8° (C_2). If C_1 was heated immediately, a crystal change occurred at 104.9–106.6° but if it were cooled to C_2 and then reheated, no crystal change was observed. Therefore, these crystals are believed to be the same (C_2). Both melted to the smectic C phase at 108° ($C_2 \rightarrow S_C$). Fresh crystals also seemed to undergo a change on heating suggesting that these are C_1. No crystal changes were observed in the C_9 homolog when the smectic C phase was cooled to 95° and reheated.

We do not usually study crystal changes as thoroughly as was done in this series since we are primarily interested in mesophases and solid polymorphism can be very complex. Quite likely, we have not observed all the changes that occur in this series. However, because of the complex melting transitions in some of these homologs, it was necessary to study these crystal changes more thoroughly. Wide range melting transitions were sometimes observed suggesting the sample was impure and the complex melting in the C_5 homolog had to be determined in order to decide whether the smectic C phase was enantiotropic or monotropic. The observance of several crystalline forms in the cyclohexane diesters **3a** is not unusual; such changes were also observed when $X = RO$.[5] Solid modifications in a few other mesogens have been studied more extensively and the results suggest that core and/or tail conformational changes occur in these transitions.[15] It would not be surprising to find more of these changes occurring in these cyclohexane diesters because of the presence of the flexible cyclohexane ring.

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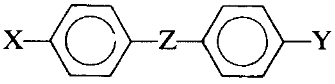
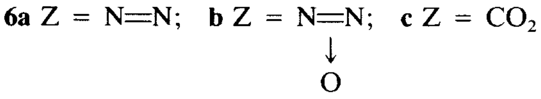
DISCUSSION

The effect of inserting an α-keto group into the phenolic chain on transition temperatures and mesophase ranges was the same in both the phenylbenzoates **4** and the cyclohexane diesters **5**. This is not surprising since the introduction of a stronger dipole into mesogens usually gives mesophases with higher transition temperatures. However, this structural modification affected the types of smectic phases differently in these two series. Only the uniaxial smectic A phase was observed in the phenylbenzoates whereas only the biaxial smectic C phase was observed in the cyclohexane diesters. No S_A–S_C combinations were observed in either series.

Early proposals for the structures of these two smectic phases suggested that the molecules in the smectic A phase are packed in a parallel manner perpendicular to the smectic layers with random distances between the molecules whereas in the smectic C phase the molecules are tilted in the smectic layers. Little is known as to why some molecules prefer to tilt in the smectic layers whereas others do not, but a number of theories have been proposed (see Reference 16 for a summary of these). Several of these theories propose that dipoles within the molecules cause them to tilt. De Jeu feels that dipoles could explain his observations that no biaxial smectic phases were observed in either the azo **6a** or azoxy series **6b**





$$\mathbf{6a}\ Z = N{=}N;\quad \mathbf{b}\ Z = \underset{\substack{\downarrow \\ O}}{N{=}N};\quad \mathbf{c}\ Z = CO_2$$

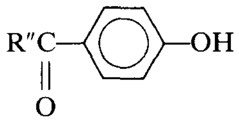
when both X and Y were alkyl, a mixture of uniaxial and biaxial smectic phases when X = alkyl and Y = alkoxy and only biaxial smectic phases (S_C) when X = Y = alkoxy.[17] A similar trend of increasing enhancement of the smectic C phase can be seen in the phenylbenzoates **6c** when X and Y are R and/or RO. Thus, the addition of an α-keto group which has a stronger dipole than the alkoxy group would be expected to favor the smectic C phase in the phenylbenzoates rather than the observed smectic A phase. However, the direction of the α-keto dipole with respect to the long axis of the molecule is quite different from that of the alkoxy dipole which might explain the observance of a S_A phase. The cyclohexane diesters **3a** also show an enhancement for tilted phases on going from Y = R (S_A, S_B) to Y = RO (S_A, S_C, S_B, S_{Biax}) and in this series this does persist into the α-keto series (S_C) as one would expect.

More recently, it has been proposed that the molecules in the smectic A phase are actually tilted but that this tilt occurs in random directions to give a uniaxial phase whereas the tilt in the smectic C phase occurs preferentially in one direction producing a biaxial phase.[18a,b] If the earlier smectic A structure is considered, then one must explain why the α-keto group favors the formation of the non-tilted smectic A phase in the phenylbenzoates but causes the molecules to tilt to give a smectic C phase in the cyclohexane diesters. If the more recent smectic A structure is considered, then the question becomes one of the tilt of the director rather than the molecules.

At this point, we do not feel enough data are available to even attempt an explanation. It should be noted, however, that there is one major difference between the structures of the phenylbenzoates **4** and the cyclohexane diesters **5**. The latter esters are symmetrical with two central groups containing dipoles along with two terminal α-keto groups with dipoles whereas the phenylbenzoates have only one central group and one α-keto group. In some way, this might be the reason for the large difference in the type of smectic phases observed in these two series. In this context, it should be noted that three well known homologous series, which have S_C phases with large tilt angles and no S_A phases, all have symmetrical or nearly symmetrical molecules and identical dipoles on both sides of the aromatic core: the dimeric 4-alkoxybenzoic acids, the dialkoxyazoxybenzenes and the *bis*(alkoxybenzal)chlorophenylenediamines.[18c]

SYNTHESIS

A variety of methods have previously been used to prepare the α-ketophenols **7**.



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The most widely used have been the Friedel-Crafts acylation of phenols with an acid chloride in the presence of $AlCl_3$[19-21] or with an acid in the presence of BF_3[22,23] and a Fries rearrangement of alkylbenzoates.[24] We tried all these methods and were able to isolate the 4-isomer but usually only in low yields. This is not surprising since Ralston and Bauer reported that yields of the 4-ketophenols are at their minimum for mid-chain length keto groups[26] which were the lengths needed in this work. Although no attempt was made to maximize yields, we were able to isolate the $R'' = C_9$ phenol in a 69% yield using a Friedel-Crafts acylation with the acid chloride in the presence of $AlCl_3$ in CH_2Cl_2. This procedure is given in the experimental section. Yields, however, depend on the ease of separating the 4- from the 2-isomer.

Most of the α-keto phenylbenzoates **4** were prepared using the acid chloride method as described in Reference 1, but a few were prepared using the carbodiimide method as described in Reference 4. Crude yields ranged from 80–90%. Some of these were purified by recrystallization from ethanol but most were too insoluble. These were recrystallized either from ethyl acetate or a mixture of this with ethanol. Purified yields ranged from 70 to 85%. The cyclohexane diesters **5** were prepared from the diacid chloride according to the method described in Reference 5. Yields were generally lower (crude 58–74%, purified 23–35%) than for the phenylbenzoates. These were even less soluble in ethanol and all were recrystallized with difficulty from various combinations of ethanol and chloroform or ethyl acetate. Characterization data for these compounds are given in the experimental section.

EXPERIMENTAL SECTION

Techniques

TLC data were obtained in $CHCl_3$ using Analtech silica gel GHLF 2.5 × 10 cm Uniplates (250 μ) with UV light as the detector. A Pye Unicam 3-200 IR instrument was used to obtain IR data and NMR spectra were determined in CCl_4 soln with TMS as an internal standard on a Varian EM-360 instrument. Transition temperatures and mesophase identification were determined 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 as described in Reference 27.

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MATERIALS

Two different sets of transition temperature data have been reported for compound **4** with R″ = C_2 and X = C_5O and C_6O with one reference reporting an unknown smectic along with a nematic phase and the other only a nematic phase[3c]. These two compounds were remade and found to have the following transitions for X = C_5O: 97.0–99.5 ($C \rightarrow S_A$), 107.5–107.9 ($S_A \rightarrow N$), 117.5 ($N \rightarrow I$) and 76 ($S_A \rightarrow C$) and X = C_6O: 86–89 ($C \rightarrow S_A$), 119.0 ($S_A \rightarrow N$), 123.3–123.4 ($S_A \rightarrow I$) and 59 ($S_A \rightarrow C$). Some new phenylbenzoates **2a** were prepared for comparison studies. Complete transition temperatures for these are as follows: X = C_{10}, Y = C_5; 38.0–39.3 (C–I), 33.3–33.4° (monotropic $N \rightarrow I$), 31.2–31.8° (monotropic $S_B \rightarrow N$) and ~14.0° ($S_B \rightarrow C$); X = C_{10}, Y = C_6, 44.5–48.4° ($C \rightarrow I$) and 33.4 ($I \rightarrow C$) and X = C_8O, Y = C_6, 52.4–53.3 ($C \rightarrow S_A$), 58.6–58.7 ($S_A \rightarrow N$), 62.1–62.9 ($N \rightarrow I$) and 32.3° ($S_A \rightarrow C$).

The 4-substituted benzoyl chlorides were prepared using methods described in the literature: X = R in Reference 28 and X = RO in Reference 29.†

4-Hydroxynonanoylphenone, 7 (R″ = C_9)

To a soln of phenol (49.3 g, 0.52 mole) in 500 ml anhyd $CHCl_2$ at <0° was added in small portions, $AlCl_3$ (139.7 g, 1.04 moles) followed by nonanoyl chloride (100 g, 0.52 mole) in a dropwise manner. This reaction mixture was refluxed 4 hr, cooled to RT, poured onto 500 g of crushed ice and extracted with 3 × 300 ml CH_2Cl_2. The organic layer was separated, washed with H_2O, dried over anhyd Na_2SO_4 and filtered. The solvent was removed from the filtrate *in vacuo* to give 129.5 g (99.6%) of the crude phenol. Recrystallization of this material twice from ligroine (bp 60–80°)-EtOH in a 6:1 ratio gave 89.7 g (69.3%) of the desired 4-isomer **7** (R″ = C_9): mp 62–64° corr (lit[30] mp 62–63°); TLC ($CHCl_3$) showed one spot with R_f = 0.08 (R_f for phenol = 0.18); IR ($CHCl_3$) 3290 (OH), 1650 (C=O) and 1600 with shoulder at 1580 cm^{-1} (Ar) and NMR (CCl_4) δ9.0 (s,1,OH), 7.95 (d,J=9 Hz, 2,ArH ortho to C=O), 6.95 (d,J=9 Hz, 2,ArH ortho to OH), 2.90 (t,J=7 Hz, 2,CH_2CO) and 2.0–0.70 (m,17,C_8H_{17}).

The phenol **7** with *R″* = C_2 is commercially available. When *R″* = C_4, the crude material was a liquid. Distillation removed the ortho isomer and the remaining para one was purified by recrystal-

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†Some of the 4-alkylbenzoyl chlorides and the 4-alkoxybenzoic acids are now commercially available.

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lization from MeOH at −75° with a treatment with Norit. The mp of 41–45° did not agree with that in Reference 19 (63°) but NMR indicated this was the correct material. When $R'' = C_7$, the para isomer crystallized from the crude product. This was removed by filtration, washed with ligroine (bp 60–90°) and recrystallized from ligroine-$CHCl_3$ to give a solid with MP = 67–69°. This differs from both literature values of 22.3° in Reference 19 and 59° in Reference 21. However, the latter value was for material that had not been recrystallized which could explain the lower melting point than what we observed. Although the para isomer could be isolated in this manner, the yield was low (23%) as compared to purification by recrystallization of the crude material as was done when $R'' = C_9$.

CHARACTERIZATION DATA

Series **4**, X = R: TLC $R_f = 0.79$ (R_f for starting phenol = 0.17); IR ($CHCl_3$) no OH, 1725 (CO_2Ar), 1675 (C=O) and 1600 cm^{-1} (Ar) and NMR† δ8.05 (d,J=9 Hz, 2,ArH ortho to CO_2Ar), 7.98 (d,J=9 Hz, 2,ArH ortho to C=O), 7.21 (d,J=9 Hz, 4H, ArH ortho to R and O), 2.87 (t,J=7 Hz, 2,$COCH_2$), 2.68 (t,J=7 Hz, 2,$ArCH_2$) and 2.2–0.7 (m, remaining alkyl). X=RO: TLC $R_f = 0.72$, IR ($CHCl_3$) no OH, 1720 (str, CO_2Ar), 1680 (str, C=O) and 1595 cm^{-1} (str,Ar), and NMR δ8.05 (d,J=9 Hz, 2,ArH ortho to CO_2Ar), 7.95 (d,J=9 Hz, 2,ArH ortho to C=O), 7.22 (d,J=9 Hz, 2,ArH ortho to ArOC=O), 6.88 (d,J=9 Hz, 2,ArH ortho to RO), 3.98 (t,J=6 Hz, 2,CH_2O), 2.88 (t,J=7 Hz, 2,$COCH_2$) and 2.1–0.6 (m, remaining alkyl).

Series **5** ($R'' = C_9$): TLC $R_f = 0.40$ (R_f for starting phenol = 0.14); IR ($CHCl_3$ or Nujol) 1760 (str, CO_2Ar) 1690 (str, C=O) and 1600 cm^{-1} (str,Ar) and NMR δ8.01 (d,J=9 Hz, 4,ArH ortho to C=O), 7.19 (d,J=9 Hz, 4,ArH ortho to ArOC=O), 2.92 (t,J=7 Hz, 4,CH_2CO) and 2.7–0.6 (m,36,C_6H_{10} + remaining alkyl). $R'' = C_2$ was too insoluble to obtain an NMR spectrum.

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†NMR data for the phenylbenzoates containing R and RO can be found in Ref. 8.

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