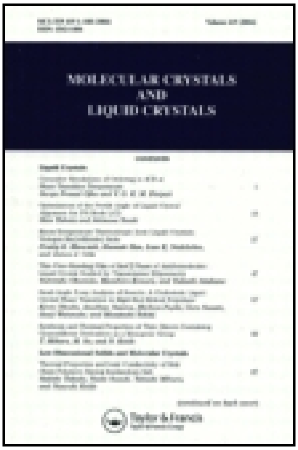

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Synthesis and Mesomorphic Properties of the Homologous Series of Di-(4′- n-alkylphenyl)-trans-cyclohexane-1,4-dicarboxylates

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Synthesis and Mesomorphic Properties of the Homologous Series of Di-(4′-*n*-alkylphenyl)-*trans*-cyclohexane-1,4-dicarboxylates†

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The homologous series of di-(4′-*n*-alkylphenyl)-*trans*-cyclohexane-1,4-dicarboxylates in which the alkyl group is C_1–C_{12} has been prepared by esterification of *trans*-1,4-cyclohexanedicarboxylic acid or dicarbonyl chloride with 4-alkylphenols. Mesomorphic properties and phase transitions as determined by hot-stage polarizing microscopy and DSC are discussed in relationship to various structural features. Comparisons of these properties with those for the corresponding alkoxy series and the analogous terephthalic acid diesters are also presented and discussed.

INTRODUCTION

Our discovery of four smectic phases (smectics A, C, B and an unidentified biaxial phase) in several members of the homologous series of di-

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(4'-*n*-alkoxyphenyl)-*trans*-cyclohexane-1,4-dicarboxylates,† **1a**[1]

1a: X = RO
1b: X = R

as compared to only two smectic phases observed in the all aromatic series,[2] suggested that smectic phases were favored by a central cyclohexane ring in this series of compounds. Thus, we were interested in preparing additional analogs as part of our continuing interest in studying the relationships between molecular properties and their smectic phases and sequences.[3,4] The dialkyl series, **1b** would be useful for comparison purposes in a study of the effect of terminal substituents on smectic properties. From known structural-mesomorphic properties relationships, this series would be expected to have lower transition temperatures and fewer mesophases than the dialkoxy series **1a**. Also of interest was whether this series would also show more smectic phases than observed in the corresponding all-aromatic series. Possibly, it would show the same smectic-to-smectic phase transition over a wide range of homologs so that a comparison could be made of the thermal parameters (ΔH, ΔS). Consequently, we prepared the series **1b** in which R = C_1–C_{12} and determined their mesomorphic properties and thermal parameters.

SYNTHESIS

The diesters were prepared by esterifying crude *trans*-1,4-cyclohexanedicarbonyl chloride with the appropriate phenol using the procedure described in Ref. 1 or by esterifying *trans*-1,4-cyclohexanedicarboxylic acid directly via the carbodiimide method (Scheme 1) as described in Ref. 4. A typical procedure is given in the experimental section for the carbodiimide method which has the advantage of avoiding working with the unstable diacid chloride. Crude yields were in the range of 82–92%.

Two methods were used to prepare the 4-alkylphenols in which R = C_3–C_{11} (commercially available material was used for R = C_1 and

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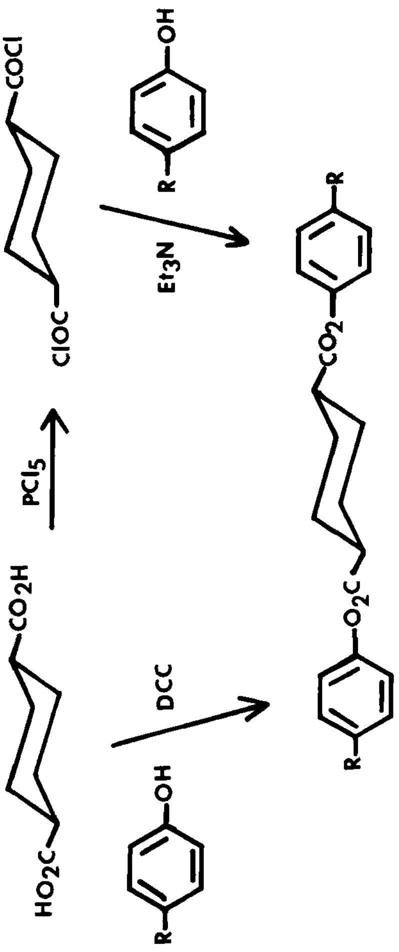
† We wish to emphasize that this is the correct name for the series we reported earlier. A correction has been made in Ref. 5, but the name originally used (actually the name for the series in which the ester groups are reversed) has occurred in several publications.



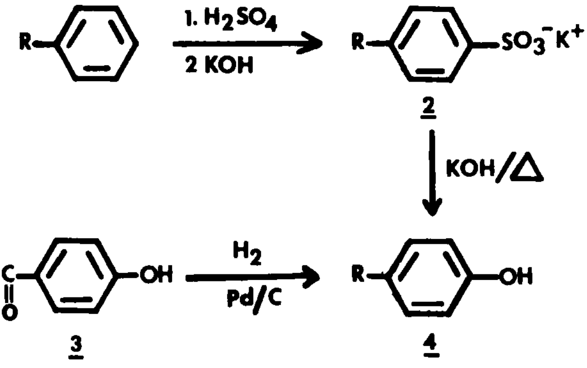
1b

SCHEME 1

C_2†). The sulfonation route (Scheme 2) was used to prepare all the phenols except the C_3 homolog. Earlier, we reported that two isolation procedures were used to obtain the sulfonates; one for shorter chain lengths and a second for longer chain lengths.[7] When $R = C_4$ or C_5, the first procedure can be used whereas the second method works better when $R \geq C_6$. However, we have now found that the first procedure cannot be used to isolate the C_3 sulfonate because of the low solubility of this sulfonic acid in chloroform. When the second method was tried, the sulfonate was too soluble in water to permit separation of it from the larger amount of inorganic salts present, i.e., the salts crystallized from solution before the sulfonate.

Infrared spectroscopy proved to be the most useful method to differentiate between the sulfonate and inorganic salts. In the pure sulfonate, a weak aromatic absorption was observed at 1620 cm^{-1} and an intense sulfonate doublet at 1210 and 1190^{-1} ‡ whereas material contaminated with inorganic salts showed a barely detectable aromatic absorption and a broad singlet at ~1200 cm^{-1}. Fusion of good quality sulfonates with potassium hydroxide gave the phenols in yields of at least 70%.

The C_3 phenol was more easily prepared by catalytic reduction of the commercially available ketone 3 (Scheme 2) in ethanol at 34°. The reduction was essentially complete within 15 minutes. With reaction times longer than an hour and at higher temperatures, noticeable reduction of the aromatic ring occurred indicating that this reduction occurs under much milder conditions than reported earlier.[8] Small



SCHEME 2

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† The phenols with $R = C_1–C_8$ are now commercially available.

‡ We neglected to record these peaks in Ref. 7.

amounts of an unidentified ketone containing material, which was difficult to remove but did not interfere with the esterification, contaminated the isolated phenol.

MESOMORPHIC PROPERTIES

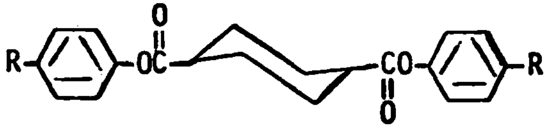
Transition temperatures and types of phases observed by microscopy for this series of compounds are presented in Table I. A comparison of the mesophase sequences for various chain lengths for the alkoxy and alkyl series is given in Table II. Interestingly, smectic phases begin to appear in both series at $R = C_4$ and the nematic phase is lost when $R = C_7$. Both biaxial phases observed in the alkoxy series are absent. Typical fan textures were observed for the smectic A and B phases with transition bars occurring in between and uniaxial crosses were found in conoscopic studies of homeotropic textures. We feel that the $S_1 \rightarrow S_2$ transition reported by Cox for the C_5 homolog[2] is actually the transition bar texture observed between the A and B smectic phases.

A plot of transition temperatures versus the number of carbon atoms in the alkyl chain (Figure 1) shows typical mesomorphic trends. The nematic-to-isotropic transition curve is a falling, odd–even alternating one which is met at $R = C_7$ by a rising smectic A-to-nematic curve beginning at C_4 with elimination of the nematic phase at C_7. A monotropic smectic B phase is also introduced at $R = C_4$ forming a slightly rising smectic B-to-A transition curve which gradually decreases the range of the smectic A phase. Extrapolation of these two curves suggests that the smectic A phase will disappear approximately when $R = C_{14}$. However, there is no indication through $R = C_{12}$ that the smectic B phase length will decrease appreciably with increasing chain length so that homologs with $R > C_{14}$ would probably have only a smectic B phase.

The melting curve is a falling one to a minimum at C_9. Not enough homologs were prepared to see a definite rising trend beyond C_9 but the slight rise between C_9 and C_{12} suggests that the curve will continue to rise beyond C_{12} and gradually decrease the phase length of the smectic B phase until it disappears. A minimum at a longer alkyl chain length than that observed in the phenylbenzoates[3] is to be expected since a longer flexible chain is needed to compensate for the longer rigid central core in this three ring system. The alkoxy series has a minimum at approximately C_{10} (Figure 2) but the absence of data for the C_9 and C_{11} homologs provides uncertainty about the exact minimum in

TABLE I

Transition temperatures (°C) and mesophase ranges for



R	C[a]	C[a]	S_B	S_A	N	I	Mesophase Range[b] Alkyl	Mesophase Range[b] Alkoxy[c]
C_1	163.8				177.2–177.7	193.1–193.5	16.3	100
C_2	98.5				111.0–111.8	161.0–161.1	50.1	103
C_3	99.7				115.9–116.0	173.5	57.6	77
C_4	71.9		(81.3–82.0)[d]	91.6–92.6	107.7–108.2	150.7–151.0	69.7	102
C_5	70.0		(90.8–92.1)	94.9–95.3	128.7–128.8	153.3–153.6	62.8	92
C_6	50.2		74.0–74.3	106.4–106.7	138.3–138.5	142.3–142.4	68.4	91
C_7	52.8		69.2–69.6	110.8–111.1	—	140.9–142.3	73.1	85
C_8	51.3	51.5	70.3–70.8	114.3–114.8	—	139.2–139.6	69.3	87
C_9	48.3		56.1	119.0–119.1	—	138.9–139.2	83.1	—
C_{10}	48.0	51.2	64.8–65.7	117.2–117.7	—	134.6–135.2	70.4	86
C_{11}	53.7		61.0–61.3	119.5–120.1	—	133.0–134.1	73.1	—
C_{12}	56.9	57.0	68.6–68.9	119.2–119.4	—	130.7–131.8	63.2	73

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

[b] Mesophase range = temperature difference between the end of the mesophase-to-isotropic transition and the beginning of the crystal-to-mesophase transition except when R = C_4 and C_5 for **1b** where it is the temperature difference between the end of the clearing transition and the beginning of the smectic B-to-A transition.

[c] Values calculated using data from Ref. 1.

[d] ( ) indicates a monotropic transition.

TABLE II

A comparison of mesophase sequences for series **1a** and **1b**

X	R	Mesophase sequence
RO	C_1–C_3	N
	C_4	N + S_A
	C_5	N + S_A + S_B
	C_6	N + S_A + S_B + S_{Biax}[a]
	C_7–C_{10}	S_A + S_C + S_B + S_{Biax}
	C_{12}	S_A + S_C + S_B
R	C_1–C_3	N
	C_4–C_6	N + S_A + S_B
	C_7–C_{11}	S_A + S_B

[a] This phase has not yet been conclusively identified.

this series. As expected, the transition temperatures for the alkyl series are lower (except the melting transition when R = C_1) than those observed for the alkoxy series. The crystallization curve (Figure 1) which represents unequilibrated melting transitions, parallels the melting curve as one would expect and does not show appreciable supercooling.

A comparison of the temperature ranges over which mesophases occur versus alkyl chain length for both series is presented in Figure 3 (see also Table I). This phase range is always less for the alkyl than for the alkoxy series although they seem to become almost identical when R = C_9. The curve is, in general, a gradually falling one for the alkoxy series whereas in the alkyl series, the curve rises at short chain lengths and seems to level off at ~C_6. There appears to be some odd–even alternating effect in this latter curve. We do not have an explanation for the large deviations from the curves at R = C_3 for the alkoxy series and at R = C_9 for the alkyl series. These curves suggest that the effect of chain length on mesophase range is greater at short chain length for the alkyl than the alkoxy series. In general, at chain lengths >C_3, a change in this length does not have much effect on the phase length until it becomes >~C_{10}.

If only smectic phase ranges are plotted as in Figure 4, both curves show a rising trend from C_4 to ~C_6, level off between C_6 and C_{10} and then fall. As with the mesophase ranges, the smectic phase ranges are always smaller for the alkyl than for the alkoxy series. Thus, these two series become more similar in their temperature ranges over which all mesophases or smectic phases specifically can occur with increasing chain length.

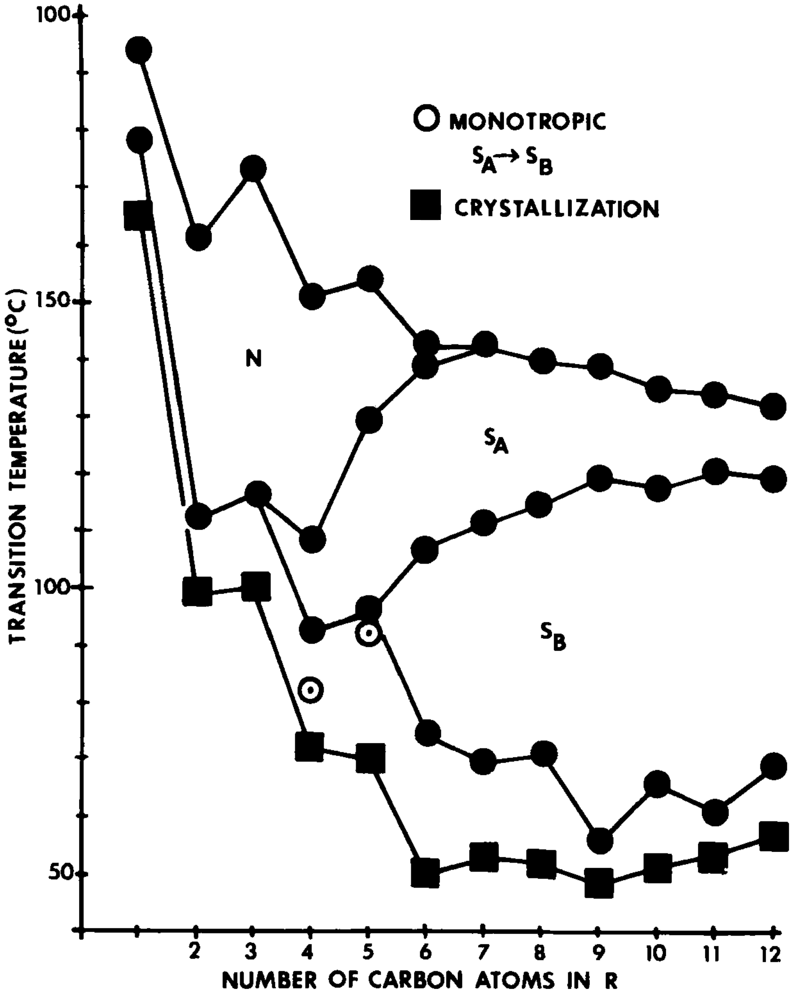
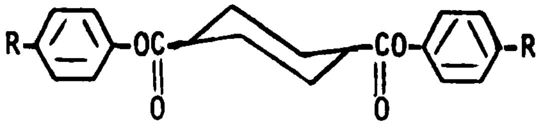


FIGURE 1 Transition temperatures versus the number of carbon atoms in the alkyl chain for



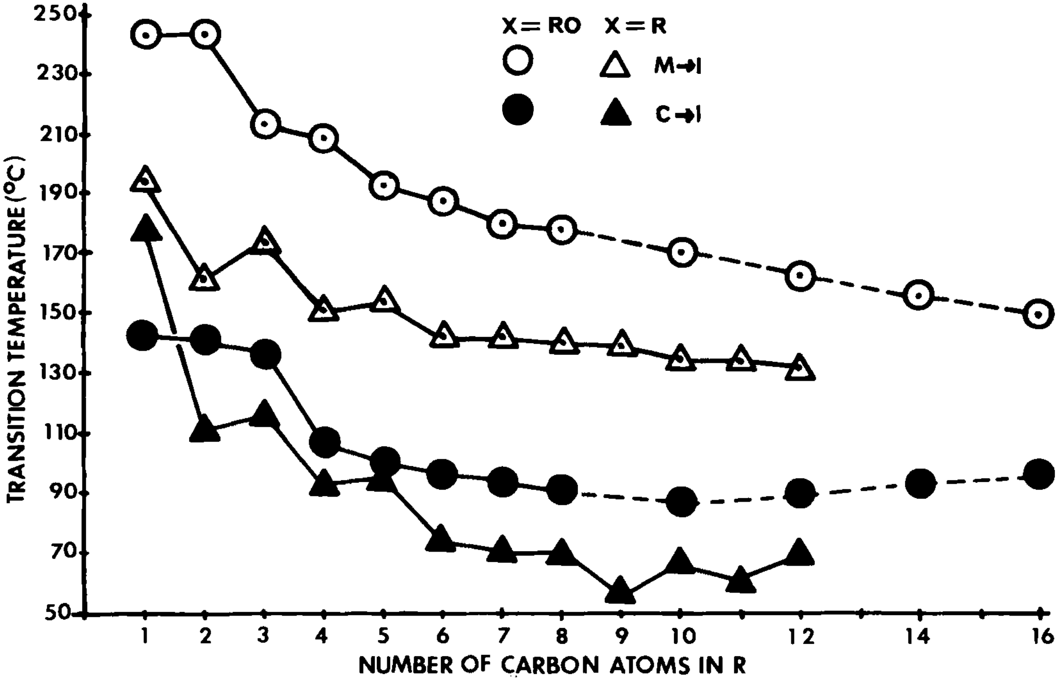


FIGURE 2 A comparison of transition temperatures versus the number of carbon atoms in the alkyl chain for **1a** and **1b**.

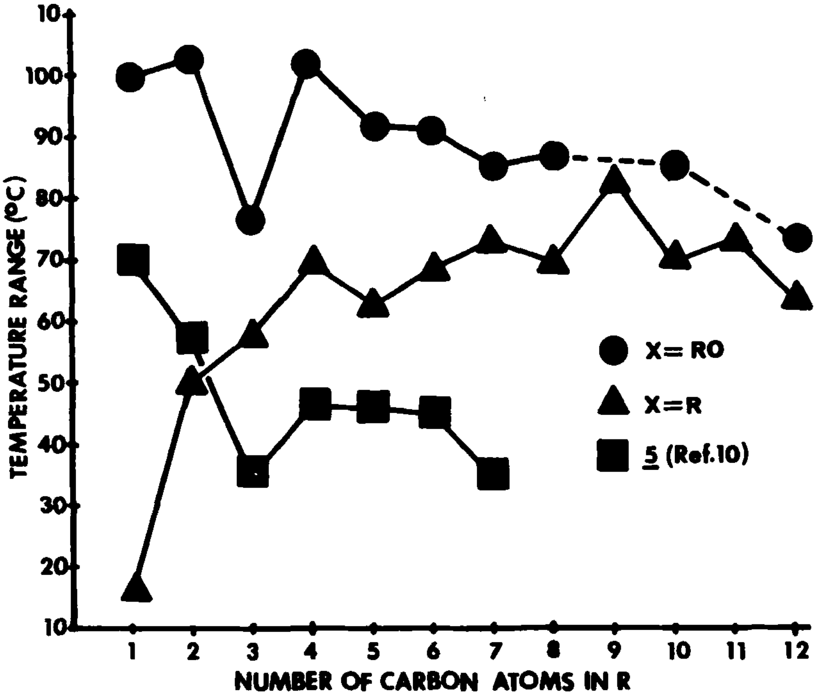


FIGURE 3 A comparison of the temperature range over which mesophases occur versus the number of carbon atoms in the alkyl chain for **1a**, **1b** and **5**.

In the alkyl series, the mesophase range is being affected only by increasing alkyl chain length. Each added methylene group increases the mesophase range until a point is reached where additional increments no longer increase this range (except when R = C_9) as increasing flexibility of the chain is balanced by the rigidity of the core (Figure 3). Beyond C_{10}, however, the flexibility becomes too great with a resulting decrease in phase length. However, in the alkoxy series, the oxygen atom on the alkoxy group adds length to the rigid core rather than to the chain because of its partial double bond character to the benzene ring. This longer rigid core is apparently more favorable for forming mesophases of longer ranges even at shorter chain lengths and appears to have a greater effect on the mesophase length than the addition of methylene groups. However, as more methylene groups are added, these serve to decrease the range slightly because of added flexibility making this series more like the alkyl one in its phase range.

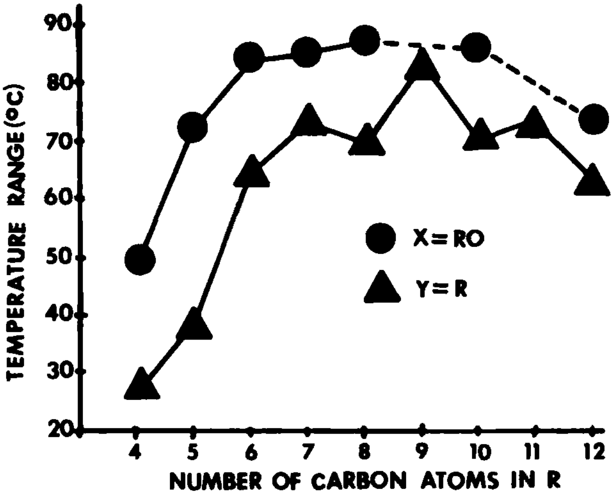
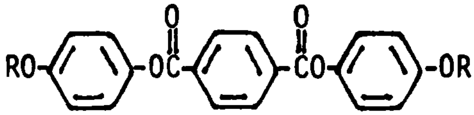


FIGURE 4 A comparison of the temperature range over which smectic phases occur versus the number of carbon atoms in the alkyl chain for **Ia** and **Ib**.

If only the smectic phase ranges are considered (Figure 4), the effect of adding methylene groups on the ranges appears to be essentially the same in both series. This would suggest that the increasing flexibility of the chain does not decrease the smectic phase range as it does the nematic range until R > C_{10}, i.e., the smectic phases can tolerate more flexibility in the tails than the nematic phases. This is not surprising since smectic phases are known to predominate at longer chain lengths and nematic phases at shorter ones.

Although the phase ranges become similar at longer chain lengths for both series, the types of smectic phases observed do not. Obviously, the presence of the ether oxygen atom in the terminal chain has quite a large effect on the types of smectic phases observed. As noted earlier, the absence of this oxygen atom leads to loss of the two biaxial phases observed in the alkoxy series. At this time, we do not have an explanation for this nor do we know how general this trend might be in series of this type. One is tempted to use this absence of biaxial smectic phases in the dialkyl series as support for McMillan's theory that outboard dipoles are needed in a structure in order to obtain a smectic C phase.[9] However, the outboard dipoles which McMillan labeled in TBBA were those in the central anil groups and not in the terminal chains. TBBA has alkyl terminal groups and still has a smectic C phase as well as several other biaxial phases.

A comparison of the mesophase ranges of these two cyclohexane diester series with those for the dialkoxy terephthalic acid diesters, **5**†



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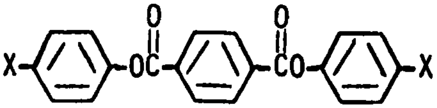
shows that the ranges for both the cyclohexane series are, in general, wider than those for the aromatic series (Figure 3). Although data for the C_5 and C_6 homologs of the alkyl all-aromatic series have been reported,[6] these transition temperatures are the same as those for the corresponding alkoxy compounds. When we prepared the C_5 homolog, we found only a nematic phase (see Table III). Apparently, a mistake was made in translating the original paper by Kelker and Scheurle.[11] However, the phase range for the C_5 all-aromatic compound is only 28.2° whereas it is 62.8° for the cyclohexane analog suggesting that the trend would be the same in a comparison of these two series.

Thus, it is obvious that those factors which favor higher transition temperatures and thus more stable mesophases do not necessarily favor the formation of smectic phases or larger temperature ranges over which mesophases can occur. It stands to reason that if this mesophase range is larger, there is a greater probability that more smectic phases can occur in this range (but not necessarily so) or that these phases will have longer phase lengths.

We remade the C_5 and C_6 all-aromatic dialkoxy esters reported by Cox‡ in order to identify the smectic phases. Our data are given in

TABLE III

Transition temperatures (°C) for



X	C	S_C	S_A	N	I
C_5O	163.3	165.4–167.6	169.7–170.4	175.0–175.5	213.9–214.1
C_6O	155.3	159.8–161.8	177.1–177.5	182.0–182.1	208.1–208.3
C_5	152.2	—	—	152.8–154.8	180.8–181.0

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† Calculated using data from Ref. 10.

‡ Cox graciously supplied us with samples of both these compounds, but we found these were too impure to obtain sharp transitions and to identify the phases. Both sam-

Table III. Both compounds have a nematic, smectic A, smectic C (with a temperature dependent tilt angle) sequence. No smectic B phases were observed. This raises the question whether the cyclohexane ring is a more favorable structural feature for the formation of smectic B phases than the aromatic ring.

DSC DATA

DSC data (Tables IV and V) were obtained for all the phase transitions observed in this series using the method described in the experimental section.

TABLE IV

Enthalpy values for transitions in compounds **1b** as determined by DSC

	ΔH(kJ mol^{-1})[a] for			
R	total C → M	$S_B \rightarrow S_A$	$S_A \rightarrow N$	M → I
C_1	35.5	—	—	1.07
C_2	30.4	—	—	0.51
C_3	34.9, 34.3[b]	—	—	0.86
C_4	27.0, 25.5[b]	1.93	0.36	0.56
C_5	35.2, 33.5[b]	2.06	0.65	0.85
C_6	30.0	2.94	2.65	1.03
C_7	30.0	2.67	—	5.45
C_8	28.0	4.09	—	6.95
C_9	51.3	4.82	—	8.00
C_{10}	64.8	5.36	—	8.63
C_{11}	35.5	6.12	—	9.51
C_{12}	57.0, 69.6[b]	6.41	—	8.71

[a] Standard deviation range = ±0.02 − ±0.10.

[b] Two slightly different melting temperatures and enthalpies were observed depending on whether fresh crystals (first value) or the crystallized melt (second value) were used. The second value was used in plotting Figure 5. The melting temperatures observed were C_3; 116.8, 116.5°C; C_4 92.8, 92.5, C_5 95.6, 95.7 and C_{12} 68.6, 68.2.

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ples gave nice nmr spectra consistent with their structures, but some insoluble solid had to be filtered from the sample solutions to obtain these spectra. This suggests that the samples contained terphthalic acid, a common problem in the synthesis of esters of this acid. We prepared our own acid chloride to be certain the material we used was all acid chloride. Using the typical procedure given in the experimental section, we were able to isolate the pure esters without the use of chromatography.

TABLE V

Entropy values for transitions in compounds **1b** determined by DSC

	S(Jmol^{-1}°K^{-1})^a for			
R	C–M	S_B–S_A	S_A–N	M–I
C_1	78.8	—	—	2.30
C_2	78.8	—	—	1.17
C_3	89.2, 88.0^b	—	—	1.93
C_4	73.7, 69.5^b	5.45	0.96	1.34
C_5	95.5, 90.9^b	5.66	1.63	2.01
C_6	86.3	7.58	6.45	2.47
C_7	84.6	6.95	—	13.16
C_8	80.9	10.52	—	16.80
C_9	156.7	12.19	—	19.36
C_{10}	191.5	13.66	—	21.03
C_{11}	106.0	15.46	—	23.30
C_{12}	166.7, 204.0	16.30	—	21.54

[a] Standard deviation range = ±0.02–0.40.
[b] See Table IV for an explanation of these values.

MELTING TRANSITIONS

A variety of crystal modifications were observed in these transitions. In the C_3–C_5 homologs, two slightly different melting temperatures and ΔH values were obtained depending on whether fresh crystals or the crystallized melt were used. Melting fresh crystals produced a major peak with a much smaller one preceding it either as a definite peak or as a broad shoulder whereas melting the crystallized melt gave a single peak, but with a slightly smaller ΔH value. The C_{12} homolog showed this same behavior but with a larger ΔH value for the peak obtained on melting the crystallized melt. Both the C_9 and C_{10} homologs showed two definite crystal modifications (Table VI) whereas the C_{11} showed

TABLE VI

Enthalpy and entropy values for crystal–crystal transitions for compounds **1b**

	$C_2 \rightarrow C_1$			$C_1 \rightarrow S_B$		
R	T(°C)	ΔH^a	ΔS^b	T(°C)	ΔH^a	ΔS^b
C_9	209.1	23.6	72.9	238.8	27.7	83.8
C_{10}	186.9	5.1	16.1	279.5	59.7	175.6

[a] kJmol^{-1}.
[b] Jmole^{-1}°K^{-1}.

two modifications, but the peaks could not be completely resolved. These transitions were not investigated further since we were primarily interested in mesomorphic transitions.

A plot of ΔS values for the melting transitions versus the number of carbon atoms in the alkyl group (Figure 5) for the alkyl series shows little variation in ΔS values except for a minimum at $R = C_4$ until

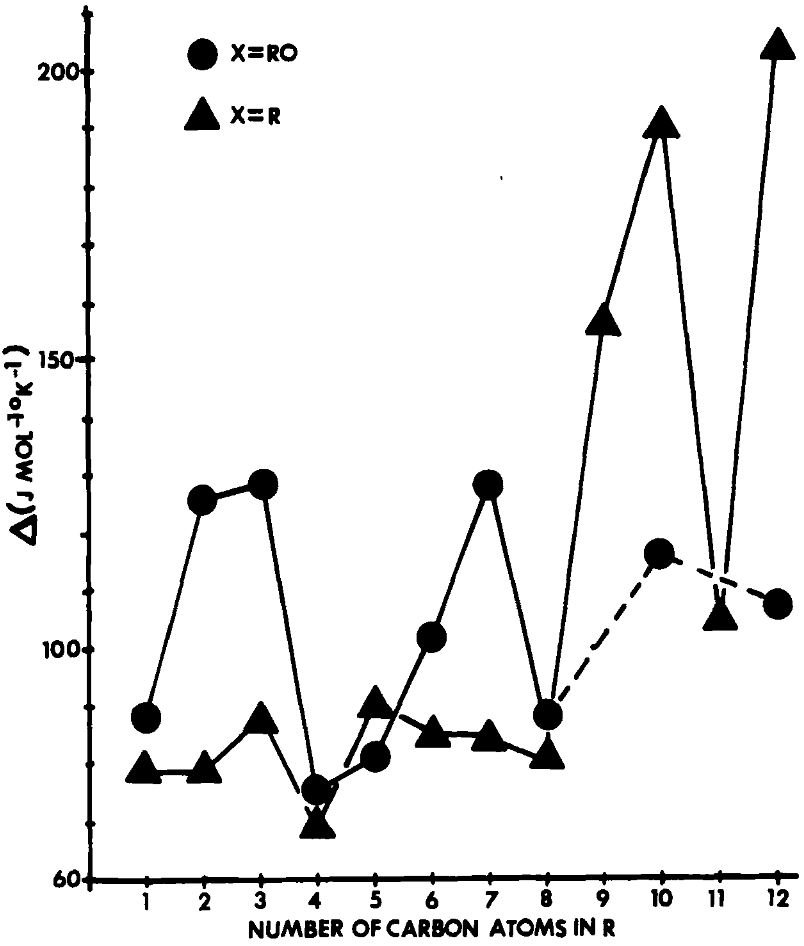

FIGURE 5 Entropy change for total crystal to mesophase transition versus alkyl chain length for

$R = C_9$. At this point, there is a dramatic increase in the ΔS values which continues until $R = C_{11}$ where the curve falls rapidly and then rises again at C_{12}. We do not have an explanation for these large fluctuations at this time. This curve is quite different from the one for the alkoxy series (Figure 5) which shows a fluctuation in values around a ΔS value of ~100. In general, ΔS values when $R < C_9$ for the alkyl series are less than those for the alkoxy series except when $R = C_5$. This larger ΔS value does not correspond to a higher melting temperature, but does correspond to a difference in transition type from crystal-to-smectic A in the alkyl compound to crystal-to-smectic B in the alkoxy analog. When $R > C_8$, the ΔS values are generally greater for the alkyl than the alkoxy series. For these homologs, the melting transition is a crystal-to-smectic B one in both series. Long alkyl chains appear to increase the disorder change involved in this transition much more in the alkyl than in the alkoxy series perhaps because the oxygen atom increases the length of the rigid central core.

A major difficulty in comparing ΔS values of melting transitions in homologous series is that the values for all the various crystalline forms present must be included which would require low temperature studies and which we were unable to do. Such a search could conceivably eliminate some of the anomalies found in these curves.

SMECTIC B-TO-A PHASE TRANSITIONS

The large number of homologs in this series containing a smectic B-to-A phase transition made it possible to plot ΔS values for this transition versus the number of carbon atoms in the alkyl chain (Figure 6). This curve shows a generally rising trend with increasing alkyl chain length similar to that observed in plots of nematic-to-isotropic transitions which are believed to reflect the effect of increasing chain length on ΔS values. The deviation from a smooth curve at C_6 and/or C_7 is difficult to explain. Not enough smectic A-to-B transitions occur in the alkoxy series for comparison of these ΔS values.

CLEARING TRANSITIONS

A plot of ΔS values for the clearing transition versus the number of carbon atoms in the alkyl chain for this series (Figure 7) shows a curve which is neither rising or falling until $R = C_7$ where it rises sharply

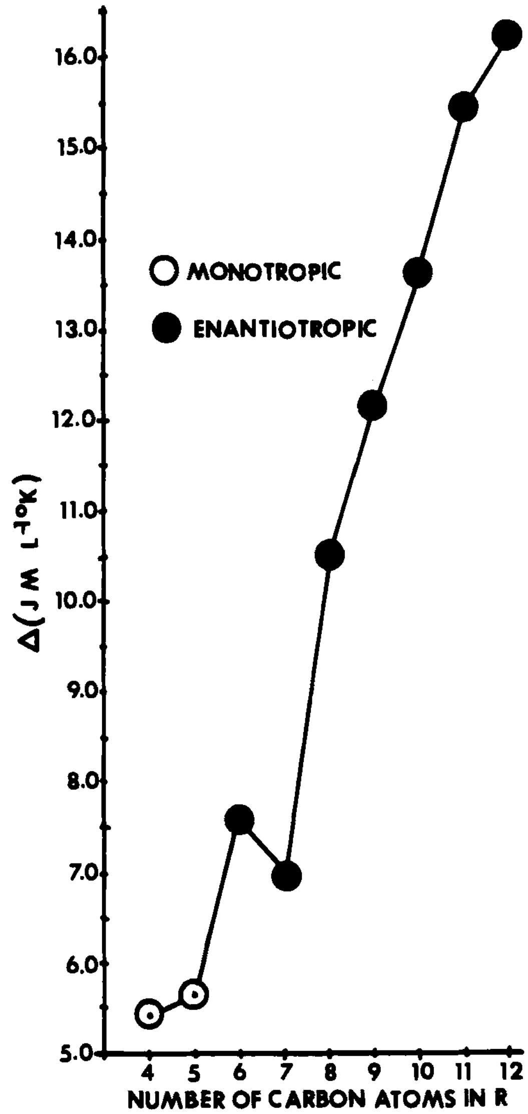

FIGURE 6 Entropy change for smectic B-to-A transition versus alkyl chain length for

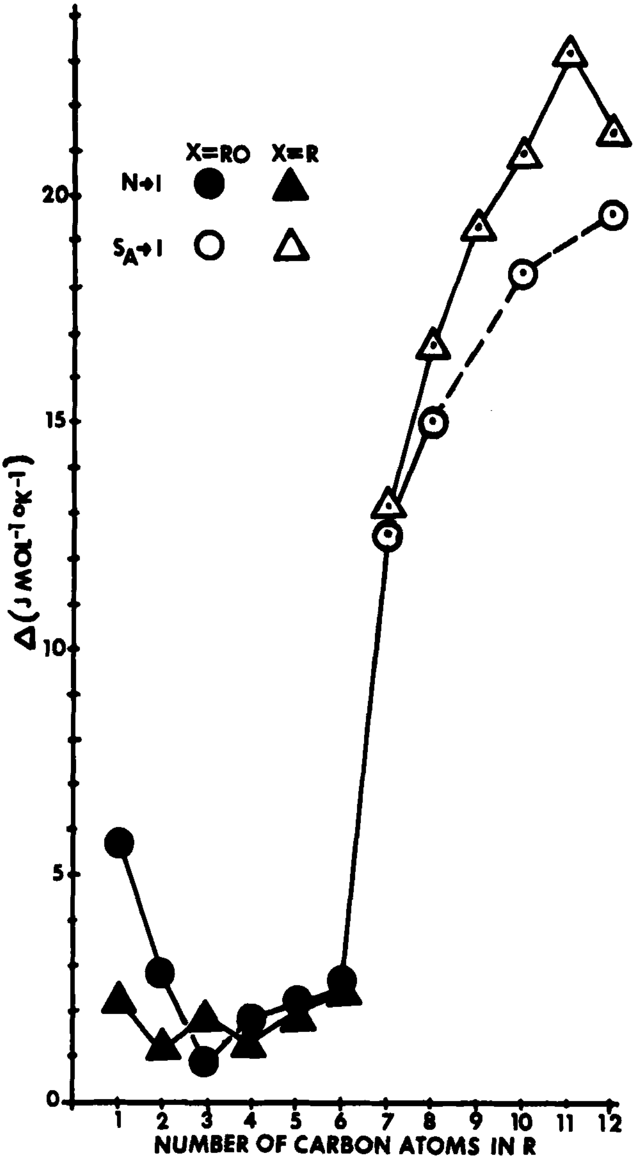

FIGURE 7 Entropy change for clearing transitions versus alkyl chain length for

with conversion from a nematic-to-isotropic transition to a smectic A-to-isotropic one. This curve continues to rise with increasing chain length until C_{12} where it begins to fall. The absence of a change in ΔS values with increasing chain length from C_1 through C_6 suggests that this length has little effect on the order in the almost liquid-like nematic phase. By contrast, the large changes between C_7 and C_{11} suggest that the smectic order is greatly affected by chain length.† The rising trend seen in both the clearing (Figure 7) and S_B-to-S_A (Figure 6) curves suggests that these smectic phases have greater order at longer chain lengths. With the lack of data for homologs $>C_{12}$, we are unable to tell whether the clearing curve will continue to fall or rise again. However, it seems likely that it will eventually fall since it is well known that mesophases are lost when the chain length becomes too long (see, for example, Ref. 3). Extrapolation of the melting and clearing curves in Figure 1 suggests that the minimum chain length at which this would occur would be C_{18}. Our experience with the phenyl benzoates suggests that this would occur at an even longer chain length.[3]

A similar plot for the alkoxy series shows an initially falling curve to a minimum at C_3,‡ a gradual rise until $R = C_6$ and then, once again, a sharp rise at C_7 when there is a change in transition type. This curve, like the alkyl one, continues to rise but at a slower rate so that the ΔS values for the alkyl series are higher than those for the alkoxy series when $R > C_7$. This indicates that the effect of chain length on the smectic order is less in the alkoxy than in the alkyl series possibly again due to the extension of core rigidity by the alkoxy group. When $R = C_7$, the ΔS values are essentially the same and thus the chain length effect. These larger ΔS values do not correspond to higher transition temperatures in the alkyl series once again illustrating that trends in these temperatures do not necessarily reflect trends in other physical parameters. Interestingly, the types of mesophase transitions involved are exactly the same for the same number of carbon atoms in the terminal chain, but not for the same number of total atoms present. This again supports the idea that the alkoxy oxygen atom acts more like part of the rigid core of the molecule than as part of the flexible chain. A comparison of Figures 5 and 7 suggests that there are larger

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† The authors appreciate the suggestions made by the referee which were used in this discussion.

‡ The referee provided this explanation: "The bulky almost freely rotating alkyl chain disrupts by a mass effect the alignment of the dipoles (real or induced) at the core of the molecule. This decreases nematic order and decreases the entropy change experienced upon clearing."

differences in the melting transitional disorder than in the clearing disorder between the two series. The effect of chain length seems to be greater for short chains for the alkoxy series but greater at long chain lengths for the alkyl series.

One must, however, be careful in comparing DSC data. Barrall and Johnson have indicated that the accuracy of DSC measurements is ±1–10%.[12] A comparison of our data for the C_1 alkoxy compound with that obtained by more sophisticated calorimetric studies[13] (Table VII) shows that the value for the melting transition is in better agreement than that for the clearing transition. This is probably due to the presence of pre- and post-transition effects observed by calorimetry which can not be detected by DSC.† This could affect the general trends in DSC data if these transitional effects varied among the different homologs.

We were also concerned that there might be a problem in comparing data from two different instruments so we obtained new DSC data for compound **1a** ($R = C_5$) using our current method. Comparisons of these data as well as Cox's are made in Table VIII. Except for the C_2 to C_3 transition all the data compares favorably. We found that this value is dependent on sample history. The lowest ΔH value was obtained when the sample was melted directly, the next highest value when this melt was allowed to crystallize and remelted and the highest value when the melt was allowed to crystallize and then kept at 5° for 44 hours before melting. The highest value corresponds to our published data and the lowest value compares with Cox's data. Thus, the prob-

TABLE VII

Comparison of ΔH values for compound **1a** ($R = CH_3$) obtained by different methods

	ΔH (kJ mol^{-1}) for	
Method	C → N	N → I
Our DSC	35.87	1.30
Andrews[a]	36.70	2.87
Cox[b]	31.68	0.97

[a] Data from Ref. 13.
[b] Data from Ref. 2.

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† The author appreciates the help of both J. T. S. Andrews and the referee in providing this explanation.

TABLE VIII

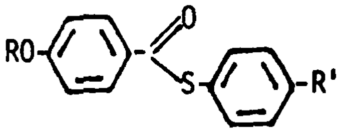
Comparison of ΔH values for compound **1a** ($R = C_5$) obtained by different methods

	H(kJmol^{-1}) for					
Method	$C_2 \rightarrow C_3$	$C_2 \rightarrow C_1$	$C_1 \rightarrow S_B$	$S_B \rightarrow S_A$	$S_A \rightarrow N$	$N \rightarrow I$
DSC-1[a]	22.0	0.59	6.51	1.16	0.72	1.04
DSC-2[b]	12.86	0.59	6.62	1.13	—	—
DSC-2[b]	15.75	0.75	5.87	1.05	0.99	0.98
DSC-2[b]	20.91	0.67	6.49	1.42	—	—
Cox[c]	12.65	0.54	5.82	1.17	1.07	1.05

[a] Data from Ref. 1.
[b] The differences in these experiments are discussed in the text.
[c] Data from Ref. 2.

lem with solid modifications appears to be a more serious one in comparing DSC data than the type of instrument used.

Despite problems with solid modifications in the melting transitions, we see some interesting trends in our DSC data for various ester series of mesogens. Although the structure of these alkylcyclohexane diesters is quite different from that for the thioesters **6**,



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both series show a minimum at longer chain lengths in their ΔH(ΔS) curves for the melting transition; at C_{11} for the cyclohexane series and at C_{12} for the thioesters.[4] Unfortunately, data for the C_{11} homolog in the alkoxy series is not available so we cannot compare this series as well. In similar curves for the clearing transitions, all three series show basically the same curve with only small variations at shorter lengths followed by a sharp rise when the transition changes from nematic-to-isotropic to smectic A-to-isotropic and then a leveling off or decrease at ~$R = C_{11}$–C_{13}. Interestingly, all three series involve the same type of clearing transition except the change from nematic-to-isotropic to smectic A-to-isotropic occurs at $R = C_{12}$ for the thioesters. These curves reflect the effect of two variables on the thermal parameters; increasing values with increasing chain lengths and sharp increases resulting from a change in the type of mesophase involved.

CONCLUSIONS

Transition temperatures for the alkyl series **1b** were found to be, in general, lower than those for the alkyl series, **1a**. Only nematic, smectics A and B were observed; no biaxial phases were found. The ranges over which mesophases or smectic phases occurred were also smaller, but these became more similar at longer chain lengths. Although this phase range in short or long chain homologs is affected considerably by the addition of a methylene group; at mid-chain length, its effect is small. Interestingly, these phase ranges were usually larger than those observed for the alkoxy all-aromatic series.

In melting transitions, ΔS values tend to be smaller for the alkyl than for the alkoxy series at short chain lengths, but larger at long chain lengths. Increasing ΔS values for smectic A-to-isotropic and smectics B-to-A transitions reflect the greater effect of chain lengths on these transitions than on nematic-to-isotropic ones. This effect was larger in the alkyl than in the alkoxy series.

EXPERIMENTAL

Trans-1,4-cyclohexanedicarboxylic acid (99%) was obtained from Aldrich Chemical Company and used without purification. Organic extracts were dried over anhyd Na_2SO_4 followed by Linde #4A molecular sieves. Anal-Tech 2.5 × 10 cm × 250 μ silica gel Uniplates® were used to obtain tlc data using UV light as the detector and $CHCl_3$ as the solvent. Spectra data were determined using a Perkin–Elmer 700 spectrophotometer for ir and either a Varian FT-80 or an EM-360 instrument for nmr with TMS as an internal standard in $CDCl_3$. The elemental analysis was obtained from Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

Transition temperatures and microscopic textures were determined using a Leitz–Wetzler ortholux polarizing microscope equipped with a calibrated, modified Mettler FP-2 heating stage at a rate of 2°/min. Samples were cooled until they crystallized. Transitions were studied using the method described in Ref. 14 unless otherwise indicated.

DSC data were obtained using a Perkin–Elmer DSC-2 instrument interfaced to a Digital Electronics Corporation PDP-11V03 minicomputer. Transition temperatures and enthalpies were determined with the aid of programs written for the DSC-2 instrument by J. T. S. Andrews. Values for monotropic transitions were determined by reheating the cooled mesophase; temperatures were obtained from the strip chart curve. Enthalpy values were calculated using the equation, $\Delta S = \Delta H/T$. An indium standard was used for calibrating the instrument and samples were weighed by difference in Perkin–Elmer aluminum pans on a Perkin–Elmer AM-2 autobalance. Scans were run at several rates (5, 2.5, 1.25 and 0.629 $K \cdot min^{-1}$) and ranges (5, 2 and 1 $mcal \cdot S^{-1}$) depending on the sample studied. Cooling curves were run to 20° below the observed crystallization before reheating. Multiple runs (1–3) with fresh samples were employed at various intervals as a check on the data obtained. Samples shown by DSC to be impure by poor peak resolution were recrystallized until satisfactory curves were obtained.

Di-(4'-*n*-butylphenyl)-*trans*-cyclohexane-1,4-dicarboxylate, 1b ($R = C_4H_9$)

To a stirred mixture of 590 mg (3.90 mmoles) of 4-*n*-butylphenol (prepared by the first method described in Ref. 7), 339 mg (1.97 mmoles) *trans*-1,4-cyclohexanedicarboxylic acid and 19 mg of 4-N,N-dimethylpyridine in 10 ml CH_2Cl_2 was added 811 mg (3.90 mmoles) of N,N-dicyclohexylcarbodiimide. The stirred reaction mixture was refluxed ~30 min., cooled, extracted with equal volumes of 3*N*HCl, H_2O, 5% aq KOH and H_2O. The organic layer was separated, dried and filtered. Removal of the solvent from the filtrate (Rotovap) gave 925 mg (quantitative) of the crude solid ester. Recrystallization of this material twice from abs. EtOH yielded 290 mg (34.2%) of the purified diester, **1b** ($R = C_4H_9$): TLC $R_f = 0.55$ (4-*n*-pentylphenol $R_f = 0.26$); IR ($CHCl_3$) 1740 (ester C = 0) and 1500 (aromatic) cm^{-1}; NMR δ7.26 (d, 4, J = 8.0 Hz, 2ArH *ortho* to ester), 7.00 (d, 4, J = 8.0 Hz, 2ArH *ortho* to C_4), 2.65 (t, J = 6.0 Hz, $2CH_2Ar$, 2.32–0.70 (m, cyclohexane and $2C_3H_7$, total integral for 2.65–0.72 represents 28 Hs).

Anal. Calcd for $C_{28}H_{36}O_4$: C, 77.03; H, 8.31. Found: C, 76.98; H, 8.27.

Di-(4'-*n*-pentylphenyl)terephthalate

A stirred mixture of 1.0 g (6.0 mmoles) of terephthalic acid and 2.5 g (12.0 mmoles) PCl_5 was heated until a liquid was obtained. Phosphoryl chloride was removed by distillation using an aspirator. A soln of 1.97 g (12.0 mmoles) of 4-*n*-pentylphenol (Eastman Kodak Co.) in 10 ml pyridine was added dropwise to the remaining solid. This reaction mixture was refluxed for 2 hr, cooled, poured into 50 ml H_2O and the resulting solid collected by filtration, washed with water and dried to give 1.43 g (52.0%) of the crude ester. Recrystallization of this material twice from $CHCl_3$- EtOH gave 840 mg (30.5%) of the desired ester: TLC $R_f = 0.69$ (4-*n*-pentylphenol $R_f = 0.26$).

Catalytic reduction of 4-propionylphenol

4-Propionylphenol (Aldrich) was recrystallized twice from abs. EtOH. A soln of 7.5 g (50 mmoles) of this material in 150 ml abs. EtOH was hydrogenated in the presence of 800 mg 10% Pd/C (Matheson, Coleman and Bell) at 50 lbs/in^2 at 34° for 50 min. The catalyst was removed by suction filtration through Celite® on Whatman No. 50 filter paper and the solvent removed from the filtrate (Rotovap) to give 7.0 g of a pinkish liquid. Distillation of this material at 103°C at 1.0 mm [lit[15] bp 79–80°C (0.75 mm)] gave 6.1 g (90%) of the purified phenol, **4** ($R = C_3H_7$): TLC $R_f = 0.16$ (starting ketone $R_f = 0.03$); IR (Film) 3350 (br, OH), 1700 (weak, unidentified) and 1600, 1610 (Ar) cm^{-1} and NMR 7.05 (s, 1, OH), 7.07 (d, 2, J = 7.9 Hz, ArH *ortho* to OH), 6.87 (d, 2, J = 7.9 Hz, ArH *ortho* to alkyl) and 2.47–0.80 (m, 7, CH_2Ar and Pr).

Acknowledgments

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