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Synthesis and Mesomorphic Properties of the Homologous Series of *trans*-1,4-Cyclohexane-di-4′-*n*-Alkoxybenzenes†

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The homologous series of *trans*-1,4-cyclohexane-di-4′-*n*-alkoxybenzoates in which the alkyl group is C_1–C_8, C_{10}, C_{12}, C_{14} and C_{16} has been prepared by esterification of *trans*-1,4-cyclohexanedicarbonyl chloride with 4-alkoxyphenols. Mesomorphic properties and phase transitions have been determined using polarizing hot-stage microscopy and DSC. A comparison of the data for this series with those for the analogous terephthalic acid diesters gives some insight into the effect of a cyclohexane ring on mesomorphic properties. Relationships between thermal and x-ray data and structures are discussed.

INTRODUCTION

The known relationships between molecular structure and mesomorphic properties have been discussed extensively by Gray.[1–3] These relationships deal primarily with those features which favor formation of mesophases, increase their thermal stability and their temperature ranges. Much more emphasis has been put on nematic rather than smectic phases because of their use in industrial applications. Little is known about the structural features which favor formation of smectic phases or the type, multiplicity and sequence of the smectics observed. Yet the large variety of known smectic phases with their different structures make these mesophases particularly interesting in studies of phase structures and transitions (see, for example, Refs. 4–8). Good structural-mesomorphism relationships would be useful in

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† Presented at the Seventh International Liquid Crystal Conference, Bordeaux, France, 1978.
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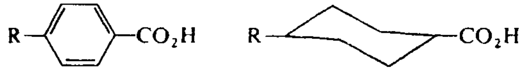
TABLE I

Comparison of the Mesomorphic Properties for *trans*-4-Alkylcyclohexyl Carboxylic Acids with those for 4-Alkylbenzoic Acids†



	Transition Temperature (°C)				
R	N	I	S_B	N	I
C_5	88	126.5		54	105
C_6	97.5	114.5	32	48	97
C_7	101.5	120	39	75	101
C_8	99.5	112.5	37	90	99
C_9	98.5	115	36	99	100
C_{10}	94.5	109	36		99

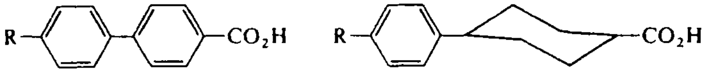
† Data from Refs. 9 and 10.

designing compounds with the types of smectic phases or interphase transitions of interest.

We were particularly interested in the observations in some series such as the acids shown in Tables I[9,10] and II[11] that replacement of a benzene ring with a cyclohexane ring enhances the occurrence of smectic phases. Yet this structural change does not always enhance smectic properties as shown by the data presented in Table III.[12] We were interested in further investigating systems which contain alicyclic rings to determine the scope of the effect of this structural change on the enhancement of smectic properties.

TABLE II

Comparison of the Mesomorphic Properties for *trans*-4-(4′-Alkylphenyl) Cyclohexane Carboxylic Acids with those for 4′-Alkylbiphenyl-4-Carboxylic Acids†

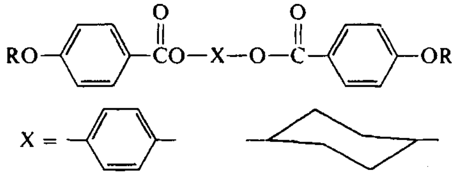


	Transition Temperature (°C)				
R	S	N	I	S	I
C_4	175.0	235.0	271.0	137.0	203.0
C_5	165.0	230.0	261.0	132.7	199.6
C_6	162.0	233.0	259.0	130.7	201.0

† Data from Ref. 11.

TABLE III

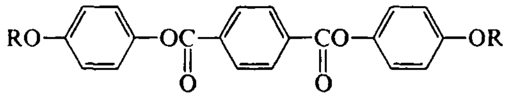
Comparison of the Mesomorphic Properties† for



	Transition Temperature (°C)			
R	N	I	N	I
C_1	222	300	(195)	197
C_4	153	241	129	157
C_6	124	213	122	136

† Data from Ref. 12.

Since mesomorphic data were already available for the aromatic esters **1**,[13] we chose to investigate the homologous series of the corresponding cyclohexane esters **6** (see Scheme 1). We were also interested in this series of compounds for use in precision adiabatic calorimetric studies of various phase transitions. Earlier calorimetric studies on the methyl homolog in this series gave better heat capacity data than that obtained for the azoxybenzenes[14]



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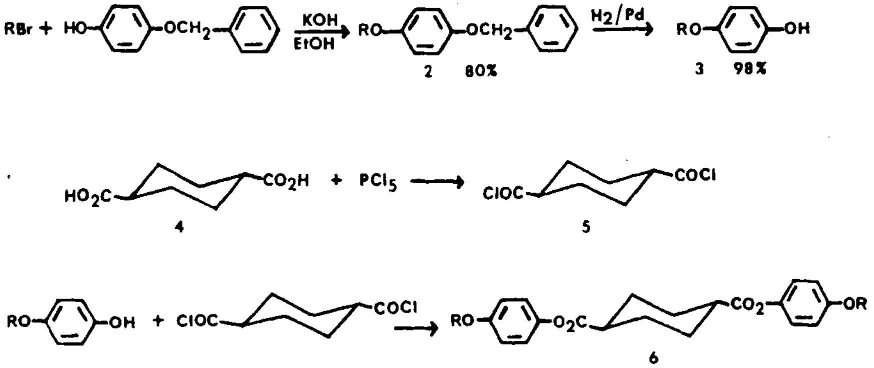


SCHEME 1 Synthesis of *trans*-1,4-cyclohexane-di-*n*-alkoxybenzoates

because of the wider temperature range of the nematic phase.[15] These esters also have the advantages of being more stable, easier to purify and reasonably accessible in large enough quantities (40–50 g) for calorimetric studies than many other series. The possibility of observing transitions involving smectic phases provided an additional incentive in that calorimetric data could be obtained on both smectic and nematic transitions.

SYNTHESIS

4-Alkoxyphenols **3** were prepared as described in detail in Ref. 16 (see scheme 1). *Trans*-1,4-cyclohexanedicarboxylic acid chloride **5** was synthesized by treating the diacid **4** with phosphorous pentachloride at ambient temperature followed by removal of the by-product, phosphoryl chloride, in *vacuo*. The remaining solid diacid chloride was not purified because of its sensitivity to moisture; good results were obtained using the crude material. An attempt to reflux the reaction mixture led to decomposition and/or polymerization. An infrared spectrum of the diacid chloride showed two carbonyl absorptions at 1790 and 1710 cm^{-1} presumably caused by the presence of two different cyclohexane conformations in solution.

Esterification of the diacid chloride **5** with two equivalents of the phenols **3** in methylene chloride using triethylamine as the base gave the diesters **6** in crude yields of 90–100%. Several recrystallizations from absolute ethanol gave the purified esters in yields ranging from 54–76%. DSC analyses of these materials gave estimated purities from 99.44–100%; accurate purity determinations were sometimes difficult because of the presence of a mesophase transition very close to the melting transition. Elemental analysis and spectral data were used to confirm the structure of the C_8 homolog.

MICROSCOPE STUDIES

Phase transitions were studied both by polarizing microscopy and differential scanning calorimetry (DSC). The transition temperatures and types of mesophases observed by microscopy are given in Table IV.

The sequence of photographs presented in Figures 1–10 for the phases observed for the C_7 homolog in a cooling cycle provides typical examples of the various textures observed. Textures were identified using both homogeneously and homeotropically aligned samples. The nematic phase often appeared as a homeotropic texture (consequently it is not shown here in the photographs) but nice fan textures could be obtained on cooling the sample into the smectic A phase. This fan texture could be retained throughout the

FIGURE 1 Smectic A phase for R = C_7H_{15}, T = 112.7°.

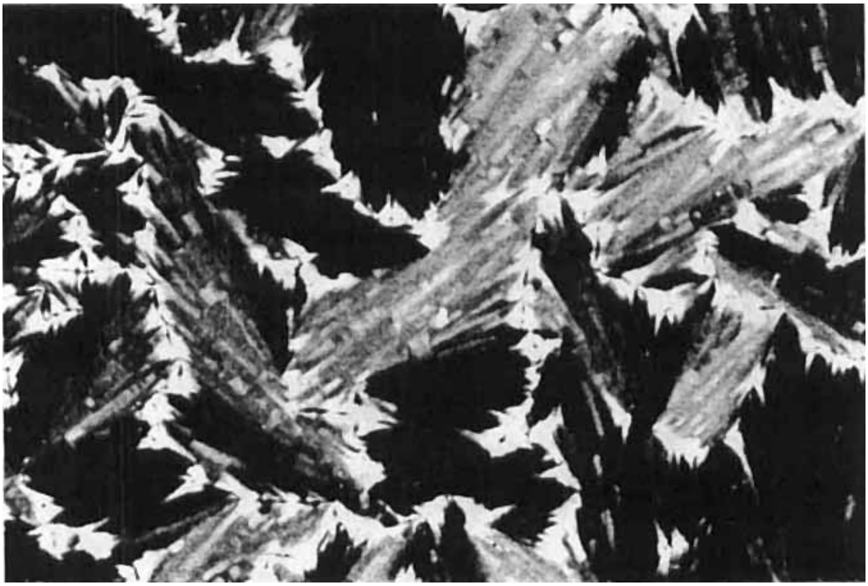


FIGURE 2 Smectic C phase for R = C_7H_{15}, T = 109.0°.

FIGURE 3 Smectic C phase for R = C_7H_{15}, T = 107.4°.

FIGURE 4 Smectic C to B transition bars for R = C_7H_{15}, T = 106.4°

FIGURE 5 Smectic B phase for R = C_7H_{15}, T = 105.4°.

FIGURE 6 Smectic 4 phase for R = C_7H_{15}, T = 95.2°.

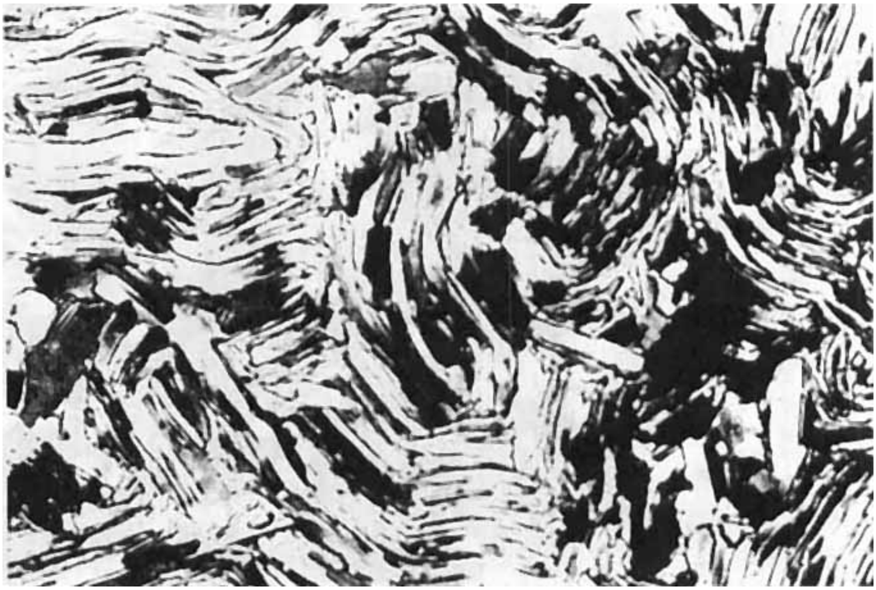


FIGURE 7 Crystal 1 phase for R = C_7H_{15}, T = 91.1°.

FIGURE 8 Crystal 1 phase for R = C_7H_{15}, T = 46.3°.

FIGURE 9 Crystal 2 phase for R = C_7H_{15}, T = 39.6°.

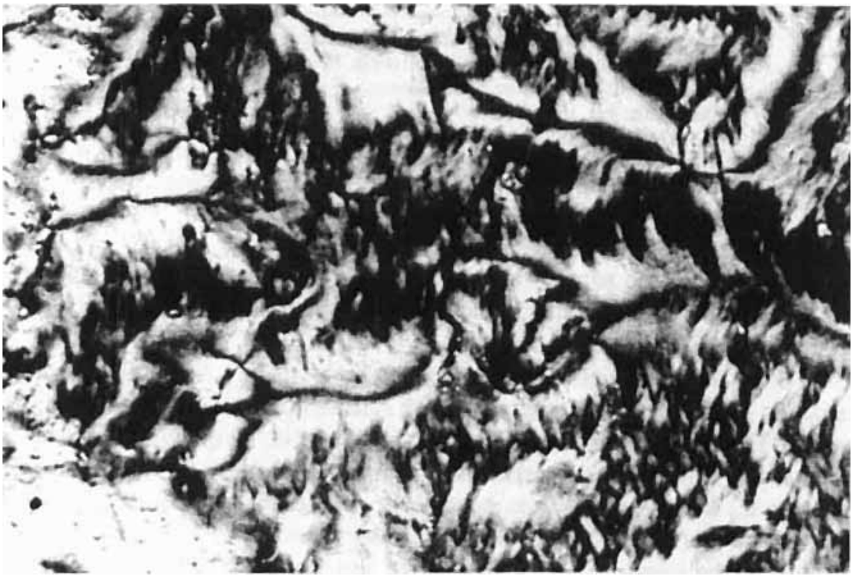
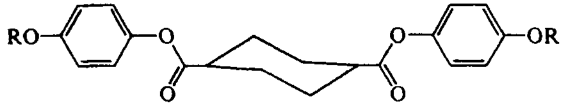


FIGURE 10 Smectic C schlieren texture for R = C_8H_{17}, T = 111.6°. (different area from Figures 1–9).

TABLE IV

Transition temperatures for



R	C_2	C_1	S_4	S_B	S_C	S_A	N	I
C_1[a]		(141)					143	243[b]
C_2		(101)					141	244
C_3		(119)					137	214
C_4[a]		(96)				107	156	209[c]
C_5	(74) $\xrightarrow{85}$	(100)		101		105	173	193
C_6	(61) $\xrightarrow{86}$	(94)	97	98		108	181	188
C_7	(36) $\xrightarrow{77}$	(88)	95	96	107	111		180
C_8	(57) $\xrightarrow{73}$	(86)	91	93	111	119		178
C_{10}		(83.6)	(83.8)[d]	87	111	146		170
C_{12}		(84)		90	112	156		163
C_{14}		(86)		94	114	155		156
C_{16}		(90)		96	115			150

( ) indicates that the temperature was obtained on cooling.

C_2, C_1 = crystalline phases, I = isotropic, N = nematic, S = smectic

[a] Compounds prepared by W. E. Bacon.

[b] Data from Ref. 15.

[c] L. Verbit and R. L. Tuggey values of 113 (C → S), 162 (S → N), 220 (N → I) in Ref. 17 and 107 (C → N), 153 (N → I) in Ref. 18.

[d] Extremely short range phase; crystallization occurred on cooling before a heating transition temperature could be obtained.

cooling cycle if the sample was not disturbed. Conoscopic studies gave a uniaxial cross for the smectic A and B phases which disappeared on going into the smectic C and smectic 4 phases.

When a smectic C phase was preceded by a smectic A, the texture of the smectic C changed in appearance with temperature as shown in Figures 2 and 3. This suggests that the tilt angle of the smectic layers in these smectic C phases are temperature dependent. This has been confirmed by x-ray studies on the C_8 homolog.[19] When no smectic A preceded the smectic C phase ($R{=}C_{16}$), this textural change was not observed so that the tilt angle does not appear to be temperature dependent in this homolog. The texture for the unknown biaxial phase also did not show this change and the lack of a temperature dependent tilt angle was confirmed by x-ray analysis.

FIGURE 11 Smectic 4 mosaic texture for R = C_8H_{17}, $T = 89.6°$. (dfferent area from Figure 10).

Transition bars were observed in the transitions between smectic A and B phases and between smectic C and B phases (Figure 4). This effect is commonly observed in transitions from either a smectic A or C phase into a uniaxial smectic B phase. Studies of homeotropically aligned regions showed black areas for the smectic A and B phases, schlieren textures for the smectic C phases (see Figure 10) and the texture shown in Figure 11 for the unknown biaxial phase, S_4. Further cooling of the texture showing the transition bars gave the typical smectic B texture (Figure 5) which on additional cooling gave a more broken fan texture for the smectic 4 phase (Figure 6).

In the homologs in which crystal-to-crystal transformations were observed ($R{=}C_5$–C_8), the first crystalline texture observed on cooling appeared as small mosaic regions (Figure 7) which slowly grew into larger regions (Figure 8) on either continued cooling (as shown in these photographs) or when a constant temperature was maintained. When no further changes occurred within this texture, further cooling gave, in a sharp transition, a second more feathery type of crystal texture (Figure 9).

The smectic C phase in the C_{16} homolog was assigned on the basis of the poor quality fan texture observed (Figure 12) which is typical of smectic C phases not preceded by a smectic A phase and by the schlieren texture observed in the non-fan textured areas (Figure 15, the area differs from that shown in Figures 12–14). Cooling the smectic C phase gave transition bars

FIGURE 12 Smectic C phase for R = $C_{16}H_{31}$, $T = 116.8°$.

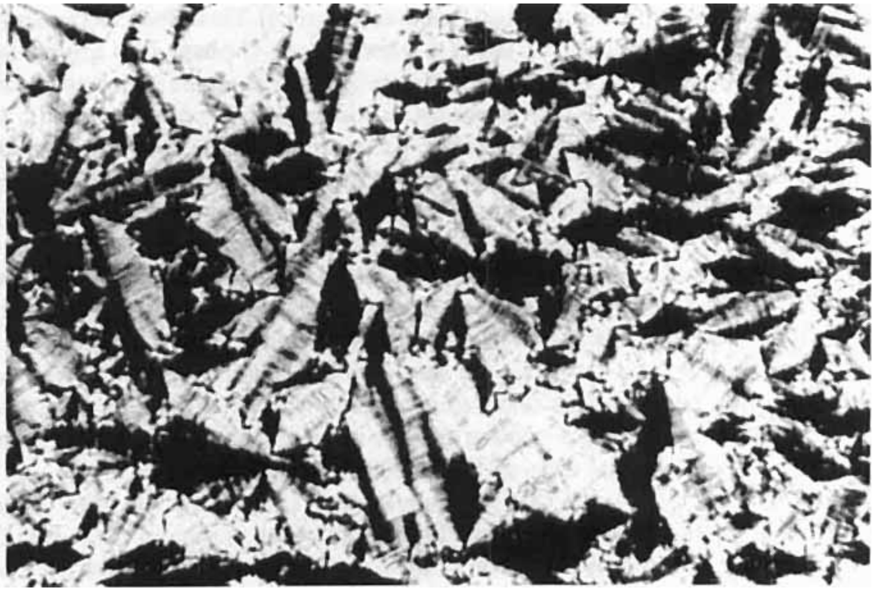


FIGURE 13 Smectic C to B transition bars for R = $C_{16}H_{31}$, $T = 113.4°$.

FIGURE 14 Smectic B phase for R = $C_{16}H_{31}$, $T = 110°$.

FIGURE 15 Smectic C schlieren texture for R = $C_{16}H_{31}$, $T = 147.9°$ (different area from that shown in Figures 12–14).

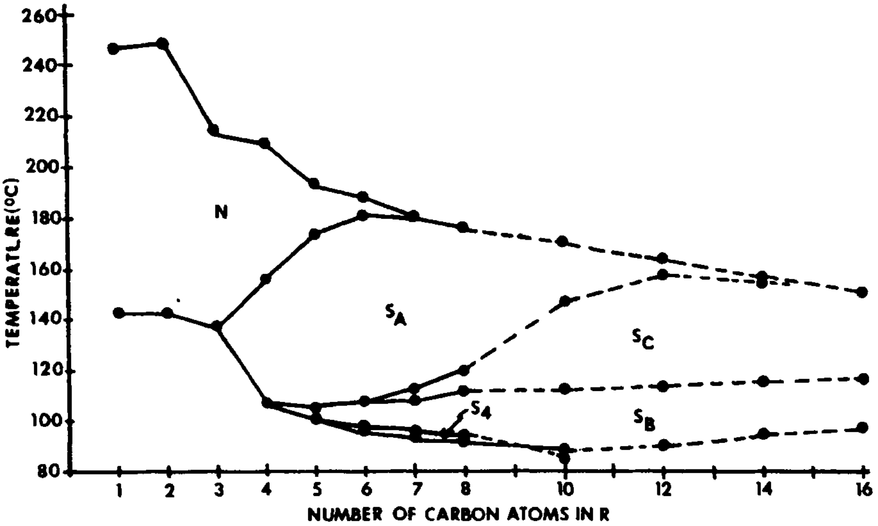


FIGURE 16 Transition temperatures as a function of alkyl chain length for

(Figure 13) followed by a typical smectic B fan texture (Figure 14). Crystallization of this material yields only one crystalline form. Conoscopic studies on a homeotropic region of this phase showed a uniaxial cross.

A plot of the transition temperatures versus chain length (Figure 16) illustrates the effect of chain length on the type of mesophases observed:

Phase	*R*
N	C_1-C_6
S_A	C_4-C_{14}
S_C	C_7-C_{16}
S_B	C_5-C_{16}
S_4	C_6-C_{10}
C_2-C_1	C_5-C_8

The smectic B to C transition temperatures are not affected much by increasing chain length and it appears that the smectic B phase will continue to occur in compounds with chain lengths $>C_{16}$. The smectic C phase length appears to decrease with increasing chain length after C_{14} but this phase would probably still occur in homologs up to about the C_{20} length. The smectic A phase, on the other hand, is lost at $R = C_{14}$. This seems to suggest that in this series, longer chain lengths favor the more highly ordered smectic

C and B phases. This is also true in the homologous series of terephthal-*bis-n*-alkylanilines.[20] However, this is not true of the even more highly ordered unknown biaxial smectic phase which in all instances occurs only over a narrow temperature range at intermediate chain lengths ($R{=}C_6$-C_{10}).

X-ray studies

An x-ray study of the C_8 homolog has been reported by A. de Vries.[19] The data suggest that the following structural features for the mesophases are present:

1) The smectic phases A, C, B are correctly assigned.

2) The molecules are tilted in the smectic A phase (angle = 17°) as well as in the smectic C and in the smectic 4 (angle = 21°) phases but in such a manner that the smectic A phase appears to be uniaxial (see Refs. 21 and 22 for more information on the structure of smectic A phases).

3) The tilt angle in the smectic C phase is temperature dependent (17 to 19°) and does not go to 0° at the smectic C to A transition.

4) The structure of the unknown biaxial smectic phase is less ordered than that found in the tilted smectic B(H) phase in TBBA (now assigned as a smectic G phase by Sackmann[23]). It's structure was tentatively assigned as a tilted smectic B phase[19] but it is now felt to be a S_F phase.[24] Further investigations of this phase using mixture studies are in progress.

5) The alkyl chains are not fully extended as is true in most other mesogenic compounds studied.

The difficulties involved in making accurate structural assignments to smectic phases, especially the more highly ordered ones was made clear by Sackmann at the Seventh International Liquid Crystal Conference.[23] Consequently, it is highly desirable to determine structural assignments by as many methods as are available. Since we have not yet performed mixture studies on these compounds, it is conceivable that some changes will be made in the structural assignments when more data become available.

Thermodynamic data

Enthalpy (ΔH, see Table V) and entropy (ΔS, see Table VI) values were determined using a Perkin-Elmer DSC-1B instrument (see the experimental section for details); more precise measurements using an adiabatic calorimeter are being determined by J. T. S. Andrews. Smectic C to A transitions were either not observed or appeared only as weak bumps on the base lines so that no enthalpy values could be obtained for these transitions. Transitions

TABLE V

Enthalpy Values for Transitions in the Compounds **6** as Determined by DSC

	ΔH (kcal/mole)[a] for				
R	total $C \rightarrow M$	S_B-S_C	S_B-S_A	S_A-N	M-I
C_1[b]	8.759				0.685
C_2	12.570				0.343
C_3	12.669				0.105
C_4	6.856			0.230	0.212
C_5	6.950		0.277	0.173	0.248
C_6	8.850		0.290	0.457	0.283
C_7	11.040	0.261			1.363
C_8	7.457	0.305			1.614
C_{10}	9.956	0.647			1.970
C_{12}	9.251	0.943			2.029
C_{14}	12.640	1.531			2.331
C_{16}	12.319	2.148			2.705

[a] Standard deviation = 0.003–0.480 kcal/mole for 3–6 runs.

[b] Data obtained from Ref. 15.

TABLE VI

Entropy values for transitions in the compounds **6** as determined by DSC

	ΔS (cal mole^{-1} °K^{-1}) for				
R	C-M	S_B-S_C	S_B-S^A	S_A-N	M-I
C_1[a]	21.1				1.36
C_2	30.1				0.66
C_3	30.7				0.21
C_4	18.1				0.44
C_5	19.4		0.74	0.05	0.53
C_6	24.4		1.01	0.39	0.61
C_7	30.5	0.68			3.00
C_8	21.0	0.81			3.60
C_{10}	27.8	1.70			4.40
C_{12}	25.7	2.50			4.70
C_{14}	34.6	4.00			5.50
C_{16}	33.5	5.60			6.40

[a] Data obtained from Ref. 15.

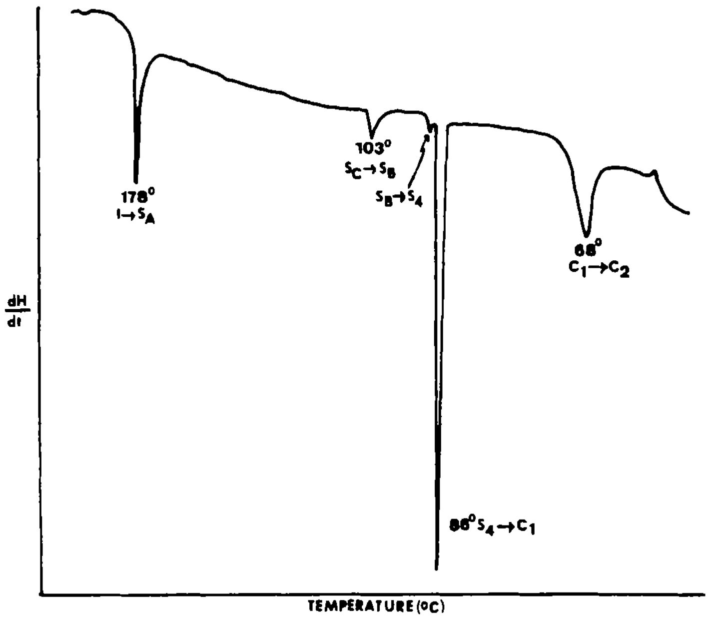


FIGURE 17 DSC cooling curve (10°/min) for

from the smectic 4 to the smectic B phase occurred over such short temperature ranges and so close to the melting transitions that these were often difficult to resolve so that separate enthalpy values were not determined. When these two peaks could be resolved (only during a cooling cycle, see Figure 17), the enthalpy values were very small.

Several solid transformations were observed by DSC that were not seen by microscopy. The data for these transitions are presented in Table VII. The

TABLE VII

Enthalpy values (kcal/mole) for melting involving crystal-to-crystal transformations

	$C_3 \rightarrow C_2$		$C_2 \rightarrow C_1$		$C_1 \rightarrow M$	
R	T(°C)	ΔH[a]	T(°C)	ΔH	T(°C)	ΔH
C_5	83.3	5.250	88.8	0.140	98.4	1.555
C_6	77.0	0.398	72.8	4.314	95.7	4.138
C_7			84.4	7.413	97.4	3.627
C_8			73.6	3.759	89.7	3.698

[a] Standard deviation = 0.002–0.275 for 3-6 runs.

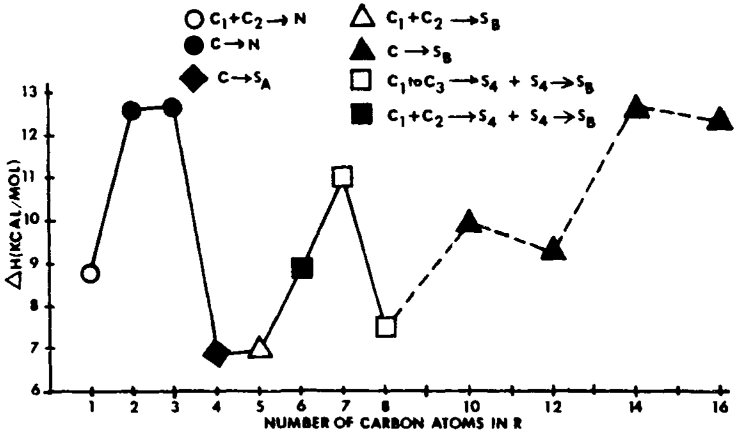


FIGURE 18 Enthalpy change for total crystal to mesophase transition as a function of alkyl chain length for

enthalpy of fusion values plotted in Figure 18 represent the sum of all the enthalpy values for all the crystal forms; more detailed data are presented in Table VII.

A plot of the enthalpy of fusion values as a function of chain length as presented in Figure 18 shows a definite but not an odd-even alternating pattern. There is no sharp rise from a minimum as is often found in similar plots of other homologous series (see for example Refs. 20 and 25). This latter behavior has been explained by the increasing flexibility of the terminal chains found in mesophases with increasing chain length over that found in the crystalline phase. Application of this reasoning to our data suggests that mesophases formed on melting in this series do not show a significant increase in the flexibility of the chains over that found in the crystalline phase as the chain is lengthened. Support for this reasoning is found in the x-ray data which suggests that the cyclohexane ring allows more room for kinking of the alkyl chains in the packing arrangement of the molecules than is found in other aromatic compounds which creates the possibility for more flexibility even in the crystalline phase.

A similar plot of the enthalpy values for the mesophase to isotropic transitions as a function of alkyl chain length (Figure 19) shows relatively constant low values (except for R=C_1) for the transitions to the isotropic liquid from the nematic phase, followed by a sharp rise when the transition occurs from a smectic A phase. This increases until the transition occurs from

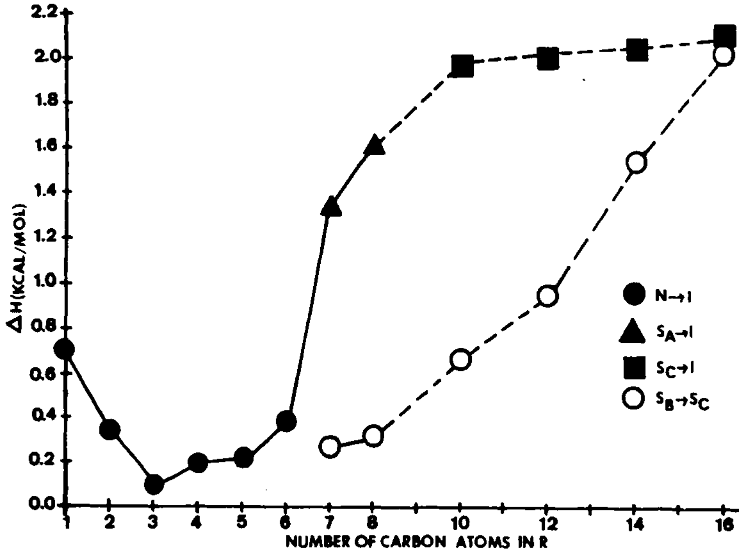


FIGURE 19 Enthalpy change for mesophase transitions as a function of alkyl chain length for

a smectic C phase at which point the curve then levels off. This merely indicates the increasing order in the three mesophases: $S_C > S_A > N$.

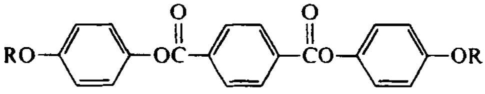
The plot of enthalpy values versus chain length for the smectic B to C transitions shows a continuous, significant rise in enthalpy values with increasing chain length. This suggests that the difference in the order in the smectic B and C phases increases with increasing chain length. This does not correspond to an increasing rise in temperature. Possibly the alkyl chains become increasingly more disordered in the smectic C phase with increasing chain length while the order in the smectic B phase remains fairly constant.

DISCUSSION

A comparison of the data for the 4-alkoxyphenyl esters of terephthalic acid (Table VIII) which possess only nematic properties with that for the analogous *trans*-1,4-cyclohexanedicarboxylic acid esters (Table IV) shows that replacement of the central benzene ring in this system with a cyclohexane ring favors formation of a variety of smectic phases even though the transition

TABLE VIII

Transition Temperatures (°C)[a] for



R	N	I
C_1	205	277
C_2	216	266
C_3	198	238
C_4	183	229
C_6	161	201
C_7	153	188

[a] Data taken from Ref. 13.

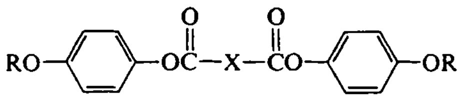
temperatures are lower. It would be unwise, however, to extrapolate this structural relationship to other systems without more extensive data on a variety of molecular structures.

Replacement of the central benzene ring with a cyclohexane ring could not increase the lateral to terminal forces ratio believed to favor the formation of smectic phases over nematics;[3] more likely there would be a decrease in this ratio. The x-ray data, which shows that the intermolecular distances are larger than with an all aromatic system, indicate that the lateral forces should be weaker in the cyclohexane series. It is also difficult to see how the dipole moments are changed in such a manner that they would be more directed across the ring than along the molecular axis than they are in the aromatic system; another factor believed to favor formation of smectic phases over nematics and particularly smectic C phases.[3]

Since the changes in intermolecular forces do not seem to be the influencing factor in determining the mesomorphic properties in this system, then apparently the cyclohexane ring must somehow have a major effect on the packing arrangement of the molecules which favors formation of smectic phases. Perhaps the increased flexibility of the central ring in the cyclohexane series allows for more possibilities in the packing arrangements of the molecules which are more desirable for forming a variety of smectic phases. Obviously, too much of an increase in flexibility would lead to a loss of mesomorphic properties altogether but perhaps some intermediate balance between rigidity and flexibility is more favorable for forming smectic phases than a rigid system. This also might be the reason why the tolanes do not show more smectic phases.[26]

CONCLUSIONS

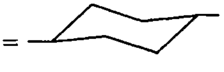
Substitution of a cyclohexane ring (**7b**) for a central benzene ring in the diesters of terephthalic acid, **7a**



7

a. X=

b. X=



leads to formation of a variety of smectic phases (S_A, S_C, S_B and $S_{F(?)}$) in addition to the nematic phase found in the all aromatic system. This suggests that such a structural change favors formation of smectic phases. Transition temperatures were lower but more mesophases were observed. At longer chain lengths smectic phases predominated over nematics while chain lengths beyond C_{14} favored the smectic C and B phases.

X-ray studies on the C_8 homolog confirmed the identification of the smectic A, C and B phases and suggests that the unknown biaxial phase is a smectic F. The intermolecular distance is greater than that found in the all aromatic system; apparently enough so as to allow the alkyl chains to kink somewhat. The tilt angle in the smectic C phase is small but temperature dependent.

A plot of enthalpy values versus chain length for the melting transitions does not show a typical rising curve but a fairly constant, alternating curve which might be due to the increased flexibility in the alkyl chains. There seems to be an increase in the difference between the orders in the smectic C and B phases with increasing alkyl chain length which might also be caused by the increased chain flexibility.

EXPERIMENTAL

trans-1,4-Cyclohexanedicarboxylic acid (99%) was obtained from Aldrich Chemical Company. Tlc was performed on 2.5 × 10 cm × 250 μ Anal-Tech silica gel Uniplates® using UV light as the detector. Crude "meling points" were determined using a Thomas–Hoover Mel-temp apparatus (Arthur H. Thomas Co.) and are corrected. Spectral data were collected using the following instruments: Perkin-Elmer 700 (ir), Varian A-60 (nmr internal TMS standard) and Associated Electronics Industries Model MS-12 (mass spec) 70 eV, 100 μA, RP $\simeq$ 1500. The elemental analysis was obtained from Spang Microanalytical Laboratory, Eagle Harbor, Michigan.

Transition temperatures and textures were determined using a Leitz-Wetzler ortholux polarizing microscope equipped with a calibrated modified Mettler FP-2 heating stage usually at a rate of 2°/min. Transitions were observed and recorded using the method described in Ref. 20 unless otherwise indicated. Photographs were taken using the microscope's Leitz 35 mm camera with Ektachrome 160 film and a 6 × objective with a 16 × eyepiece except for Figures 10, 11 and 15 where the combination was 10 × 32. All photographs within a sequence were taken at the same magnification and without moving the slide so as to maintain the same area as much as possible unless otherwise noted. More details on obtaining good fan textures are presented in Ref. 20.

DSC data were obtained using a Perkin-Elmer DSC-1B instrument interfaced to a minicomputer (Digital Equipment Corporation, model PDP-11V03). Peak area integrations, used to determine enthalpy and purity values, were performed on the computer using programs derived from the Perkin-Elmer DSC-4 program (Perkin-Elmer, Norwalk, Conn., U.S.A.).

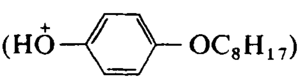
The DSC instrument was calibrated using indium standards and has been checked for agreement with known values (see Ref. 27). Temperatures were corrected using separate calibration curves for the upper and lower ranges of the instrument and agreed well with the microscope values. Entropy values were calculated using the equation, $\Delta S = \Delta H/T$.

Samples were weighed by difference on a Cahn RG electrobalance and sealed into aluminum calorimetric cells. Multiple DSC measurements were usually done on one sample (or several if necessary) with different scanning rates (5, 2.5 and 1.25°/min) and ranges (4.2 and 1 mcal/sec). The enthalpy and purity values reported here represent average values of theses determinations.

trans-1,4-Cyclohexanedicarbonyl Chloride, 5

A solid mixture of *trans*-1,4-cyclohexanedicarboxylic acid (86.1 g, 0.50 moles) and PCl_5 (208 g, 1.00 mole) was stirred cautiously at room temperature (maintained with an ice bath) for 30 min. Phosphoryl chloride was then distilled at 38° under an aspirator vacuum. The remaining colorless solid dicarbonyl chloride, 5 (100.7 g, 97.0 %) was not purified before use: ir ($CHCl_3$) 1790 (COCl, greatest intensity) and 1710 (COCl) cm^{-1}, no acid OH absorption. A mass spec showed no parent peak (m/z 210, 208) but peaks at m/e 175 (210, ^{37}Cl, 2.76 %), 173 (208, ^{35}Cl, 9.69 %) and a base peak at 81 (cyclohexane). The starting diacid spectrum had a parent peak at m/z 154 (17.69 %) and a base peak at m/z 81. The peak at m/z 154 was not observed in the spectrum for the acid chloride. This material had to be stored *in vacuo* when not in use in order to avoid hydrolysis to the acid.

trans-1,4-(4'-*n*-Octyloxyphenyl)cyclohexanedicarboxylate, 6 ($R = C_8H_{17}$)

A solution of the crude *trans*-cyclohexanedicarbonyl chloride (25.2 g, 0.12 mole) in 250 ml CH_2Cl_2 was added dropwise over 30 min to a stirred soln of 4-*n*-octyloxyphenol (53.5 g, 0.24 mole) and 33 ml (0.24 mole) Et_3N in 400 ml CH_2Cl_2 and stirred for 1.5 hr. The reaction mixture was washed with 2 × 300 ml H_2O, 2 × 250 ml 5% aq. KOH soln and 2 × 450 ml H_2O, dried over anhyd. Na_2SO_4, filtered and the solvent removed (Rotovap) to give 66 g (94%) of the crude ester **6**: mp 157–167°, tlc (CH_2Cl_2) showed two spots with $R_f = 0.63$ and 0.26 (phenol $R_f = 0.27$). Recrystallization 3 times from abs EtOH gave 52.1 g (74.4%) of purified material: tlc showed only one spot; ir ($CHCl_3$) 1740 cm^{-1} (CO_2R) and no OH absorptions; nmr ($CDCl_3$) δ6.89 (s, 8, 2ArH), 3.90 (t, 4, J = 6 Hz, $2ArOCH_2$) and 2.80–0.70 (m, 40, cyclohexane and 2-$C_7H_{15}O$); and mass spectrum (m/z) 581 (M^+, 1.54%), 359 (M^+-222, 3.33%) and 2.22 ().

Anal. Calcd. for $C_{36}H_{52}O_6$: C, 74.4; H, 9.02. Found: C, 74.46; H, 9.13.

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