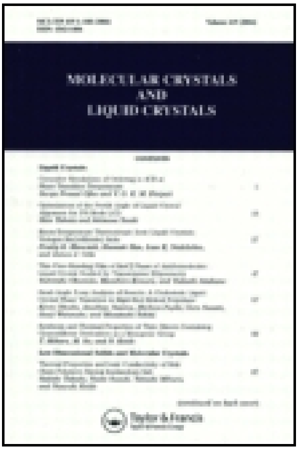

Molecular Crystals and Liquid Crystals

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Synthesis and Thermal Analysis of Fourteen Homologous Mesogenic Monoesters of Biphenyl-4,4'-dicarboxylic Acid

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Synthesis and Thermal Analysis of Fourteen Homologous Mesogenic Monoesters of Biphenyl-4,4'-dicarboxylic Acid

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We have synthesized fifteen homologous di-*n*-alkyl (dimethyl through di-*n*-pentadecyl) esters of biphenyl-4,4'-dicarboxylic acid. None of these is mesomorphic. However, monohydrolysis of the upper fourteen homologues yielded monoesters all exhibiting polymesomorphism. The phase transitions have been studied by differential scanning calorimetry and four mesophases exhibited by this series have been tentatively identified by hot-stage polarized microscopy.

1 INTRODUCTION

The factors which promote liquid crystallinity in thermal mesogens have been discussed in depth.[1,2] The biphenyl and terphenyl moieties are found in many liquid crystalline compounds. The long, linear, and rigid aromatic ring system contributes to the thermal stability of mesophases, although mesogenic compounds containing central alicyclic groups, notably *trans*-1, 4-cyclohexyl groups, are well established.[3] Terminal carboxylic acid or ester moieties seem to favor the formation of the smectic versus the nematic phase, particularly if the alkyl portion of the ester is long.[1]

Less well understood are the mechanisms that promote polymesomorphism. Also, predictions of *which* mesophases will be observed in a given

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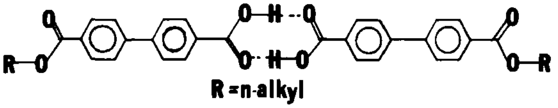
compound, based on molecular structure, are difficult. The quantity, quality, and diversity of information on liquid crystalline compounds has increased so greatly in recent years that it may begin to be possible to attempt to identify specific features of molecular architecture which favor the formation of specific mesophases.

In the effort to understand these features, it is important to compare only structurally very similar compounds. If the replacement of one moiety by another results in no significant changes in mesomorphic behavior, one is led to believe that the structural perturbation did not greatly affect the factors initially important to the formation of a particular mesophase. Similarly, if a significant change in mesomorphic behavior *does* occur on substituting one moiety for another, one is led to suspect that a factor key to the formation of a given mesophase has been affected by the change in molecular structure.

In the following sections, we describe the synthesis of fourteen homologous *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid, generically depicted as

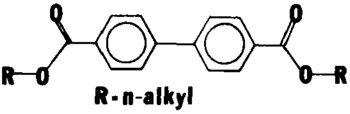


and subsequent analysis by differential scanning calorimetry and polarized hot-stage microscopy. We have tentatively identified, by optical means, four principal mesophases exhibited by these compounds, and have compared our findings with those obtained by other workers on structurally similar compounds. Although we encountered unanticipated difficulties in the study of the monoesters of biphenyl-4,4′-dicarboxylic acid, the relatively facile synthesis and the polymesomorphism observed promises to make them of considerable interest to other workers in the field of liquid crystals.

2 SYNTHESIS

Biphenyl-4,4′-dicarboxylic acid was either purchased commercially or prepared from the corresponding dibromide by lithiation and carbonation. Lithiation of 4,4′-dibromobiphenyl in dry THF with a slight excess of *n*-butyllithium at −100°C for 15 minutes, followed by carbonation in a slurry of dry ice and ether, suction filtration, acidification, and reprecipitation afforded a 70% yield of diacid very slightly contaminated with 4-bromobiphenyl-4′-carboxylic acid, isolated as an alkyl ester.

Biphenyl-4,4′-dicarboxylic acid was esterified by one of three procedures to give the diester generically depicted:



The dimethyl and diethyl esters were conveniently prepared *via* the diacid chloride in a well-known procedure.[4] The *n*-propyl and *n*-butyl diesters were prepared by Fischer esterification. The *n*-pentyl through a *n*-pentadecyl diesters were prepared by coupling the disilver salt of biphenyl-4,4′-dicarboxylic acid with the appropriate *n*-alkyl bromide.[5,6] The recrystallized diesters were purified by column chromatography. The ethyl through *n*-butyl diesters were eluted from a silica column of about 500 theoretical plates using various mixtures of ether and hexane. The diesters of higher carbon chain length were passed through a charcoal column with THF, and again recrystallized. Melting points and elemental analyses of the diesters were as follows: methyl, 218°C (71.31% C, 5.20% H); ethyl, 111.5°C (72.37% C, 6.06% H); *n*-propyl, 80°C (71.84% C, 6.91% H); *n*-butyl, 45°C (74.17% C, 7.54% H); *n*-pentyl, 40°C; *n*-hexyl, 52°C; *n*-heptyl, 57°C (76.51% C, 8.71% H); *n*-octyl, 68°C (77.43% C, 8.98% H); *n*-nonyl, 71°C (78.12% C, 9.21% H); *n*-decyl, 79°C (78.03% C, 9.68% H); *n*-undecyl, 79°C (78.60% C, 9.81% H); *n*-dodecyl, 87°C (79.02% C, 10.01% H); *n*-tridecyl, 88°C (79.16% C, 10.40% H); *n*-tetradecyl, 90°C (79.35% C, 10.60% H); and *n*-pentadecyl, 91°C (79.63% C, 10.71% H). Thin-layer chromatography (TLC) on 0.2 mm silica plates, using a mixture of ether and hexane as eluent, revealed an immobile impurity in small quantities in the *n*-heptyl, *n*-octyl, and *n*-undecyl diesters. This might be the corresponding monoester. The *n*-heptyl monoester additionally showed trace contamination by a compound more mobile than the diester. None of the diesters exhibited liquid crystalline behavior.

Following a procedure presented by Hickinbottom,[7] each *n*-alkyl diester except the diethyl was added to one equivalent of potassium hydroxide dissolved in a minimal amount of the corresponding *n*-alkanol and the mixture was stirred at room temperature. After several hours, stirring was discontinued, and the low-boiling *n*-alkanols were removed under vacuum. The higher-boiling *n*-alkanols were removed by treatment with ether. The solid remaining was acidified and recrystallized from a mixture of THF and hexane, or THF and water. Recrystallization was repeated until TLC on silica, using a 75:25 v/v mixture of chloroform and methanol, indicated the level of impurities to be at or below the detection threshhold.[8] The ethyl, *n*-propyl, and *n*-pentyl monoesters were sublimed at 195°C and 5 mm Hg to remove an immobile impurity suspected to be biphenyldicarboxylic acid, and again recrystallized. An attempt to purify the *n*-butyl monoester by liquid chromatography on silica, using a mixture of chloroform and methanol as eluent, resulted in loss of material, possibly by hydrolysis. Yields of monoester from diester approximated 50%.

The ethyl diester could not be conveniently monohydrolyzed in ethanol, and was therefore prepared using refluxing THF as a solvent. The yield was poor. Efforts to monohydrolyze the dimethyl ester failed in our hands.

Elemental analyses of the *n*-alkyl monoesters were as follows: ethyl 71.23%

C, 5.17% H; *n*-propyl 71.54% C, 5.59% H; *n*-butyl 72.40% C, 5.84% H; *n*-pentyl 72.82% C, 6.70% H; *n*-hexyl 73.61% C, 6.94% H; *n*-heptyl 74.23% C, 6.99% H; *n*-octyl 74.37% C, 7.34% H; *n*-nonyl 74.97% C, 7.67% H; *n*-decyl 75.18% C, 7.98% H; *n*-undecyl 75.69% C, 8.14% H; *n*-dodecyl 75.96% C, 8.39% H; *n*-tridecyl 76.43% C, 8.55% H; *n*-tetradecyl 76.71% C, 8.71% H; *n*-pentadecyl 77.19% C, 8.98% H.

3 DIFFERENTIAL SCANNING CALORIMETRY

Samples were placed in a desiccator at least eight hours prior to analysis on a Perkin-Elmer DSC-2 instrument equipped with a strip chart recorder. The temperature scale of the DSC-2 was calibrated daily against standard samples of indium, lead, and 99.9% benzoic acid (Fisher Brand Thermetric Standard, lot 701300). Two to six fresh samples of benzoic acid, sealed in nested sample pans, were used as enthalpic standards. About three fresh samples of each monester were scanned at rates ranging from 1.25 to 10°/minute. The temperature range of each transition was established by heating at a minimal rate, typically 1.25°/minute. Sample and standard sizes were varied over a wide range, but identical instrumental settings were maintained. The objective of these precautions was to eliminate systematic error due to day-to-day variation in instrumental response and linearity of instrumental response. The recorder output was photocopied, and the peaks excised and weighed to determine the enthalpy of each transition. We attempted to compensate for changes in the heat capacity by extrapolation of the baseline to a common point of intersection or to the midpoint of the transition.[9]

The calorimetric analysis was difficult, and the uncertainty associated with enthalpies of transition consequently large. As is noted in the following section, the monoesters are prone to both sublimation and decomposition above about 220°C, preventing the pre-annealing of the samples. The lower homologs sublime so readily that the sample pan often ruptured; the ethyl monoester invariably ruptured the sample pan. Because the samples cannot be pre-annealed, because the lower temperature mesophases are extremely viscous, and—in some cases—because two transitions could not be resolved, transitions from the crystalline phase are broad. The error in determining the area representing ΔH of a transition increases with the breadth of a transition due to error in drawing the baseline, and so the uncertainty of ΔH in some of the transitions from the crystal is very large.

We encountered one additional difficulty, apparently not previously mentioned in the literature, in treating the data obtained for the enthalpy of transition. A number of transitions exhibited a linear dependence of response (peak area/mg sample) on scan rate. Using the F-test,[10] we were able to demonstrate the existence of this effect at confidence levels exceeding 99% in three cases, exceeding 95% in five cases, exceeding 90% in eight cases, and approaching 90% in three additional cases. A number of other cases exhibited values of F weakly suggestive of a relationship between scan rate and response. It is possible that, in this last group, the dependence is masked by nonlinearity in the dependence or by random error. We are uncertain of the cause of the relationship between scan rate and observed response, but chose to attempt to correct for it by performing a least squares analysis in all cases in which the variance could not be completely explained by random error, then interpolating along the least squares line to the value of response at a scan rate of 2.5°/minute. In other cases, we used a simple average of the values obtained.

The values we obtained for the temperature range over which a transition is manifest, the enthalpy of that transition, the uncertainty in the enthalpy of that transition expressed as a 90% confidence limit, and the entropy of that transition are presented in Table I and, graphically, in Figures 1-3. Although the 90% confidence limits given in the fourth column of Table I are perhaps a pessimistic indicator of the accuracy of the results, we emphasize that the experimental difficulties that we encountered suggest that these limits are appropriate.

To exclude the possibility that the four transitions from 340°-400°K of the *n*-heptyl and *n*-octyl monoesters could be artifacts of heating from the solid state, we repetitively scanned a sample of both monoesters, packaged in a sample pan with a crimped cover, at 2.5°/minute on a DSC-1B instrument. Indium was used as the calibrant. On reheating a sample, the lowest temperature transition of each monoester was either not observed, or was found to have a diminished enthalpy of transition. The properties of the remaining transitions were not altered, implying that the solid nucleates with difficulty, and the monoesters supercool below that transition temperature. The average values obtained for those transitions examined using the DSC-1B are recorded in Table I, placed in parentheses adjacent to thoses values obtained on the DSC-2. The correspondence between the enthalpic values obtained in the two studies is good, particularly considering that the studies differ in instrument, calibrant, sample size, sample container type, and sample thermal history. Also, of course, the DSC-1B exhibited a significantly smaller signal-to-noise ratio than the DSC-2.

As revealed by Figure 2, the total enthalpy of transitions from K to I of the *n*-butyl to *n*-pentadecyl monoesters form an alternating pattern originating in the overall K to S_{II} process. The ethyl and *n*-propyl monoesters, which do not conform to the alternating pattern, do not exhibit a stable S_{II} phase. The *n*-butyl monoester, which exhibits only a narrow range of stability for the S_{II} phase, does not conform well to the alternating pattern. The remaining monoesters conform extremely well to the alternating enthalpic pattern. Linear least squares analysis[10] on the homologs with an even number n of carbons in

TABLE I

Monoester	Transition Range (°K)	ΔH (kcal/mol)	Uncertainty in ΔH (%)	ΔS (cal/mol °K)
ethyl	504.1–507.1	2.98	>20	5.89
	515.3–518.7	3.52	>20	6.81
	539.1–541.7	0.559	15	1.03
	541.7–543.7	0.814	5.5	1.50
n-propyl	433.0–440.7[a,c]	1.12	>20	2.57
	479.2–485.9	2.60	18.3	5.38
	540.9–544.4	2.39	8.8	4.41
n-butyl	408.4–419.0[b]	1.67	12	4.04
	457.1–460.7	1.33	3.4	2.91
	471.9–475.8	1.96	2.4	4.14
	502.3–504.8[b]	0.054	>20	0.109
	528.2–535.2	3.12	>20	5.87
n-pentyl	389.6–401.8	2.87	17	7.26
	421.5–430.4	1.87	10	4.38
	474.3–477.4	1.76	8.0	3.69
	503.3–510.6	0.185	20	0.364
	525.3–533.0	2.78	7.5	5.25
n-hexyl	357.1–361.3	1.11	>20	3.09
	392.5–399.4	1.12	5.4	2.82
	472.7–473.7	1.50	8.6	3.17
	513.6–515.6	0.280	>20	0.544
	520.5–524.5	2.30	15	4.40
n-heptyl	363.2–372.2	4.93 (4.46[d])	10	13.4
	380.2–384.1	0.275 (.378)	>20	0.720
	385.3–389.3	0.117 (.240)	>20	0.302
	389.6–393.6	0.202 (.210)	>20	0.516
	471.4–473.6	1.52	5.1	3.22
	515.0–515.9	0.244	>20	0.474
	518.3–522.2	2.60	12	4.99
n-octyl	340.8–348.7	1.02 (1.18[d])	15	2.95
	350.4–357.7	0.872 (.657)	>20	2.46
	372.6–378.6	0.0617 (—)	>20	0.164
	381.3–390.4[c]	1.56 (1.56)	6.0	4.05
	469.7–472.7	1.56	>20	3.30
	509.2–518.9	3.61	0.2	7.01
n-nonyl	360.3–368.6	4.76	—[d]	13.06
	378.3–383.0	1.82	0.1	4.78
	467.3–468.5	1.63	13	3.49
	508.3–511.2	2.92	2.3	5.74
n-decyl	358.9–363.3	2.29	8.4	6.33
	374.6–377.6	3.34	4.1	8.87
	463.7–466.3	1.48	7.6	3.19
	503.7–509.2	2.45	>20	4.84
n-undecyl	371.9–378.6	9.12	1.2	24.3
	464.6–469.5	1.56	8.1	3.33
	505.5–508.4[c]	3.32	11	6.56
n-dodecyl	367.7–370.8	1.83	>20	4.96
	375.6–378.3	4.47	—[d]	11.9
	378.8–381.0	0.589	—[d]	1.55
	460.4–461.3	1.39	11	3.02
	500.9–503.3	2.76	>20	5.49

n-tridecyl	380.8-386.3	10.72	4.0	27.96
	457.2-459.7	1.52	6.8	3.31
	497.7-498.7	0.394	7.8	0.791
	499.8-502.0	2.35	0.6	4.70
n-tetradecyl	371.0-377.3	1.85	0.9	4.95
	379.2-382.1[b]	6.46	2.5	17.0
	452.8-458.2	1.83	6.2	4.01
	487.0-489.1	0.350	3.9	0.717
	495.1-498.3	2.41	20	4.85
n-pentadecyl	380.6-387.1	11.7	1.9	30.6
	455.8-456.8	1.67	10	3.66
	486.2-487.3	0.367	20	0.754
	496.3-497.9	2.19	3.7	4.40

Values in parentheses in the third column are those obtained using a DSC-1B instrument and crimped sample pans, rather than a DSC-2 instrument and nested sample pans. [a] Transition range determined at 10°/min. [b] Transition range determined at 5°/min. [c] Two unresolved transitions. [d] Single value.

the pendant alkyl chain indicates that these compounds obey the equation $\Delta H = 0.777n + 1.93$, and the homologs with an odd number of carbons in the pendant chain obey the equation $\Delta H = 0.721n + 5.36$, where ΔH is the total *K-I* enthalpy of fusion. The correlation coefficients are 0.982 and 0.956, respectively. The same pattern occurs in the entropies of transition, as is evident in Figure 3.

4 HOT-STAGE POLARIZED MICROSCOPY

Observations of the thermal behavior of monoester samples were made on a Bausch and Lomb polarizing microscope equipped with a Kofler hot stage, and recorded by a Polaroid camera. Observations were complicated by the sublimation and decomposition of samples above 220°C, by the extremely high viscosity of some of the phases observed at lower temperature, and by the narrow temperature range of stability exhibited by some of the mesophases. The first-mentioned difficulty precluded identification of the mesophases shown by the ethyl monoester. We found that rapid cooling from the isotropic phase permitted the observation of the mesophases found above 220°C, although extensive decomposition occurred in a time on the order of minutes. Deposition of samples from isotropic solution in various mixtures of THF and diglyme was the best method of sample visualization at lower temperatures.[11] If the latter procedure was used, the sample was kept at a constant temperature, without a cover slip, for up to 10 hours to allow the solvent to volatilize before the texture was recorded. Stable textures without the use of a

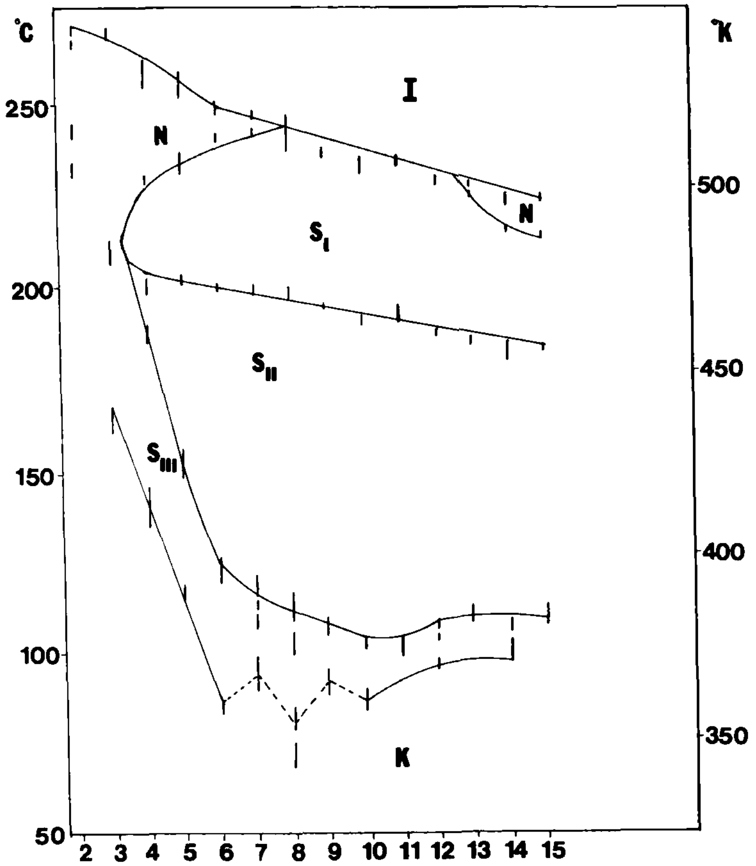


FIGURE 1 The phase transition temperatures for fourteen homologous *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid. The horizontal axis lists the number of carbons in the alkyl chain. The left-hand vertical axis is the temperature in °C and the right-hand axis is in °K. Vertical lines in the diagram represent the temperature range of a transition as given by DSC. The K-S_{III} phase region is bounded by a dotted line for several homologs because textural phenomena are too ambiguous to permit identification of the mesophase by visual means.

solvent were obtained only if the sample was maintained at constant temperature for up to a week.

The *n*-propyl, *n*-pentyl, and *n*-heptyl monoesters, if cooled from the isotropic phase between crossed polarizers, produced droplets showing Maltese crosses characteristic of the nematic phase. Although the *n*-tetradecyl and *n*-pentadecyl monoesters, if so treated, had a strong tendency to form homeotropic preparations, a well-defined, freely-flowing schlieren texture could sometimes be observed. A transient, freely-flowing schlieren texture was observed on cooling isotropic preparations of all monoesters from *n*-octyl to

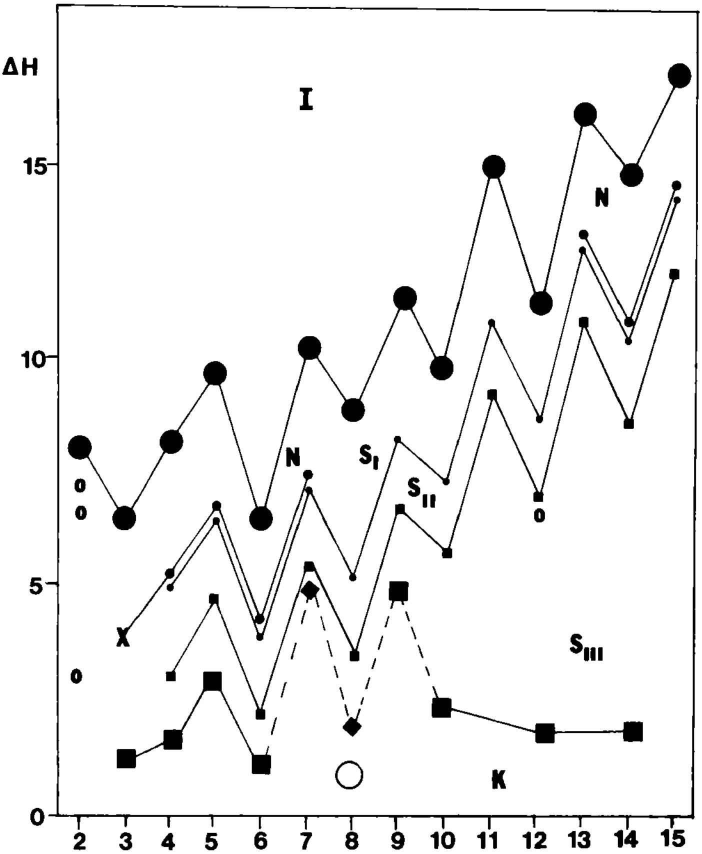


FIGURE 2 and 3 Symbols: O *K*-*K* transition; ■ *K*-S_{III} transition; ▪ S_{III}-S_{II} transition; • S_{II}-S_I transition; ● S_I-*N* transition; ●*N*- or S_I-*I* transition; **O** transition type unknown; ◆ multiple transitions; **X** S_{III}-*N* transition. The horizontal axes of both of these figures list the number of carbons in the alkyl chain. The dotted line in these figures indicates that visual examination of the mesophase texture did not permit unambiguous identification of the mesophase.

FIGURE 2 The *net* enthalpy of transition *from the crystal* into a specified mesophase for fourteen homologous *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid. The vertical axis is ΔH in kcal/mole.

n-dodecyl except the *n*-decyl; the *n*-decyl monoester decomposed almost instantaneously. For the *n*-propyl monoester, we were also able to obtain a homeotropic preparation apparently evidencing surface inversion lines. These observations lead us to identify this phase as the nematic, and to suggest that it may persist, even if not resolved by DSC, for all homologs. This region is marked *N* in Figure 1.

The characteristic texture of the region labelled S_I in Figure 1 is a blurred,

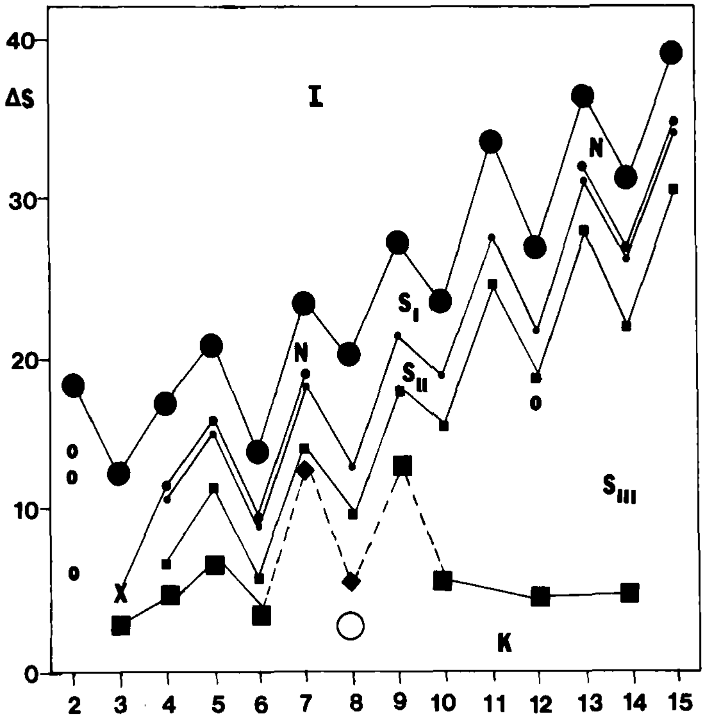
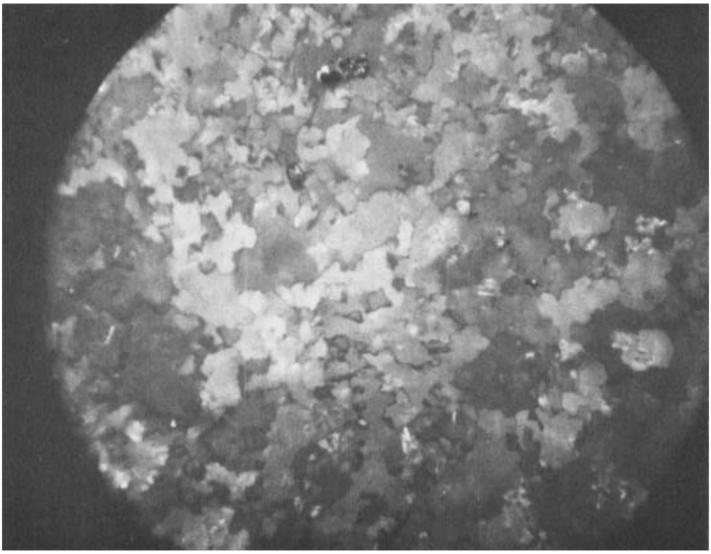


FIGURE 3 The *net* entropy of transition *from the crystal* into a specified mesophase for fourteen homologous *n*-alkyl monoesters of biphenyl-4,4'-dicarboxylic acid. The vertical axis is ΔS in cal/(mole- °K).

slowly-flowing schlieren texture. This texture may be obtained either by cooling the isotropic liquid or by deposition from diglyme. The *n*-undecyl monoester, whether cooled from the isotropic liquid or deposited from diglyme, formed a texture containing ellipses, as is shown among the photomicrographs. On the basis of these observations, we believe that S_I is probably a smectic *C* phase.

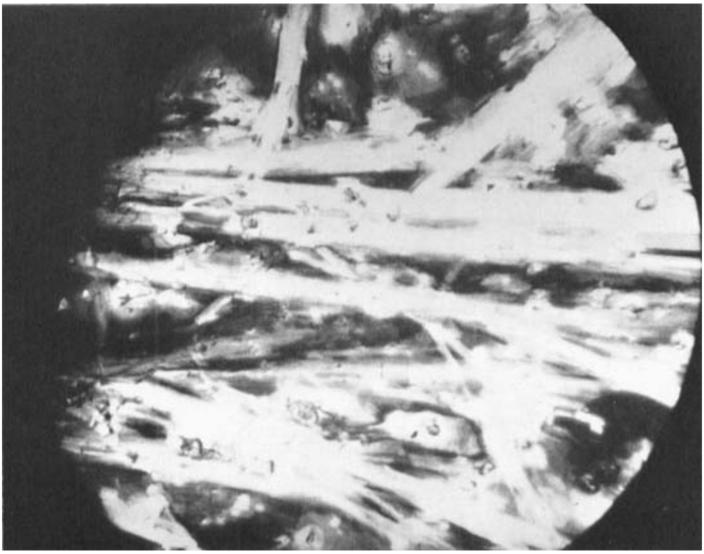
The characteristic texture of S_{II}, exhibited among the photomicrographs, is a mosaic. The texture lacks regions of homeotropy, and does not form stable terraces. Birefringence colors were not observed in those homologs examined. Brown and Wolken[12] present a photomicrograph of a mesophase which strongly resembles S_{II}, and identify that mesophase as S_B. We identify S_{II} as S_B also.

The region labelled S_{III} exhibited a mosaic texture, clearly terraced, and apparently lacking regions of homeotropy. The *n*-pentyl monoester, if deposited in S_{II} from a mixture of THF and diglyme, then slowly cooled into the S_{III} regions, first developed bright lines, apparently creases in the surface of

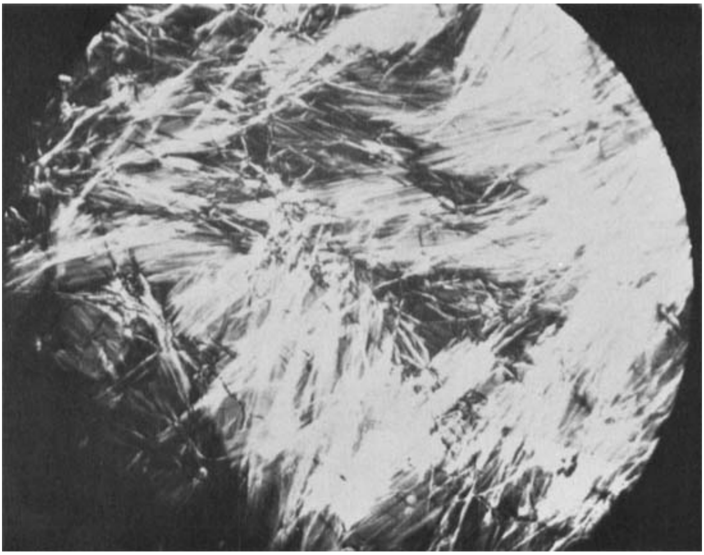


A. (i)

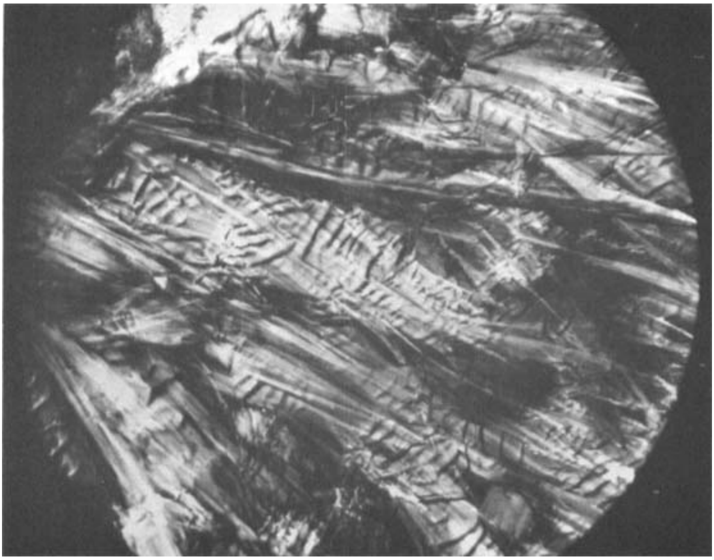
A. (ii)



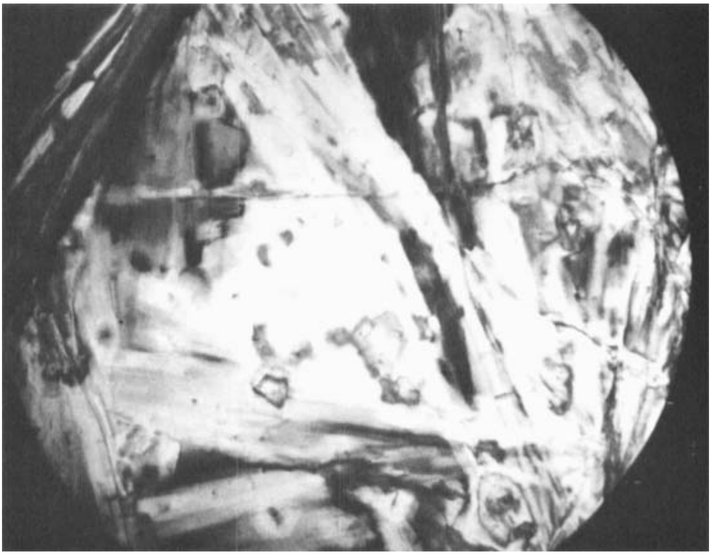
A. (iii)



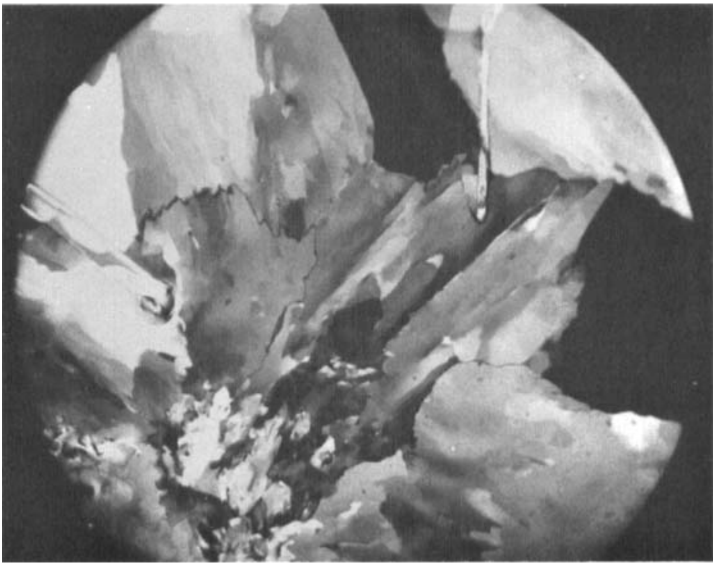
A. (iv)



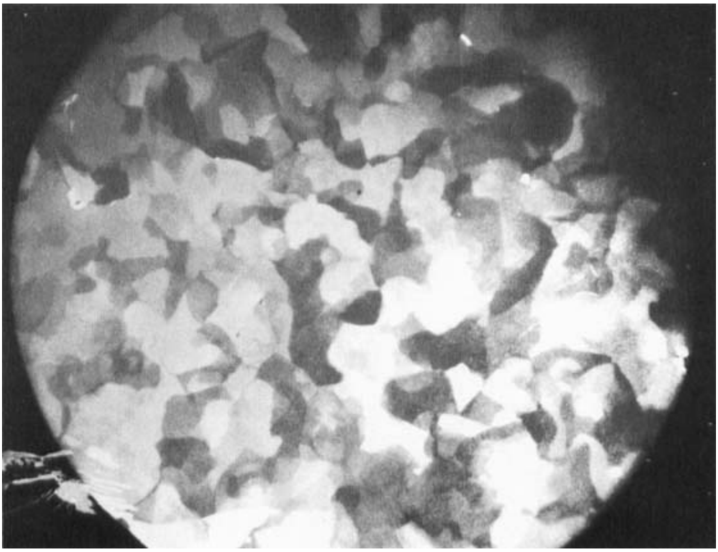
A. (v)



A. (vi)



A. (vii)



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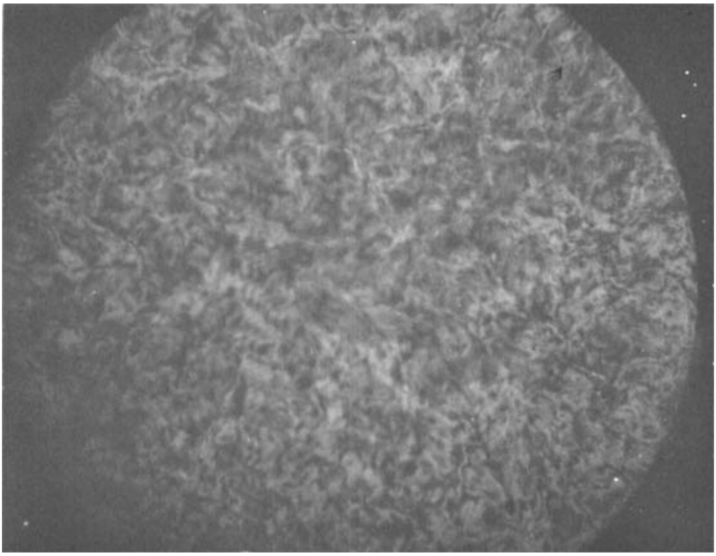
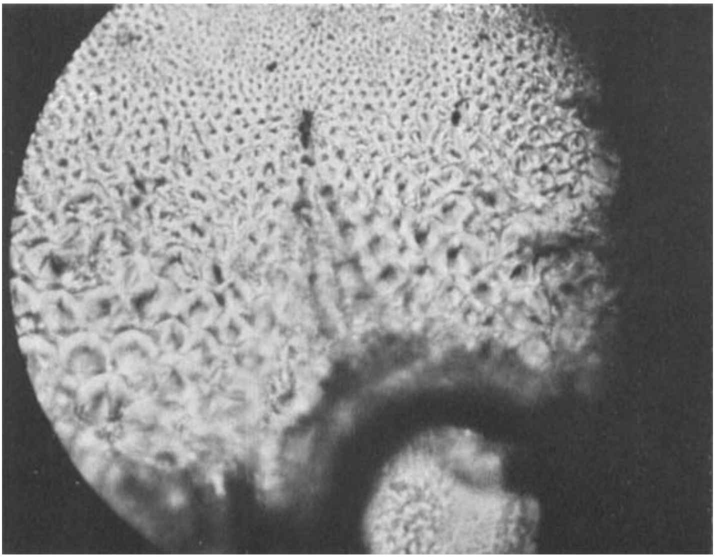
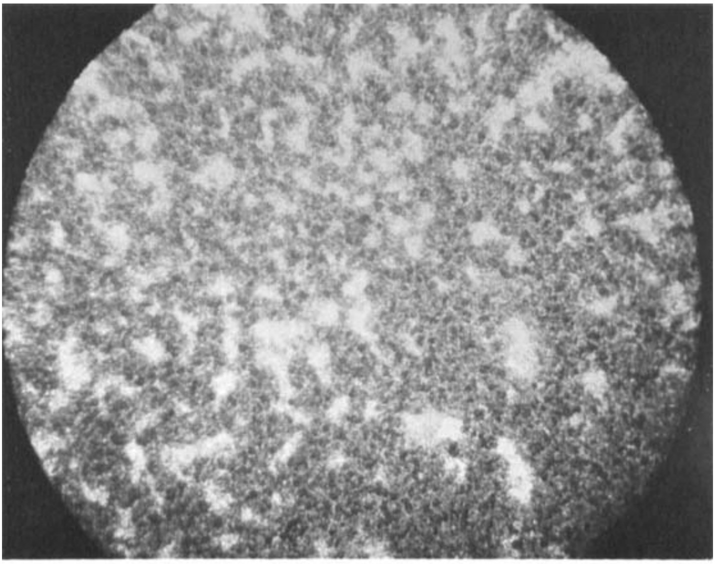


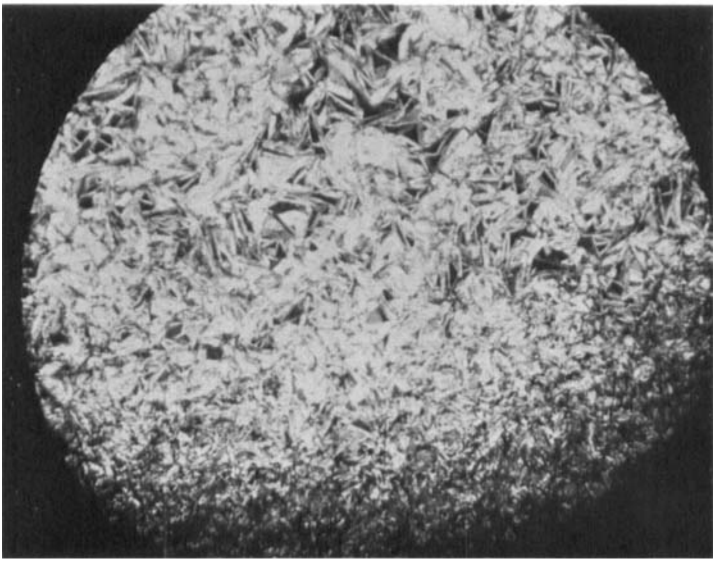
C.



D.



E.



F.

the preparation. With passage of time, these disappeared, and the sample formed a mosaic strongly resembling that shown by the *n*-tetradecyl monoester at 105°C. The *n*-pentyl monoester, if deposited from diglyme in the S_{III} region, produced first the texture shown among the photomicrographs. The features of this texture then broadened into a strongly birefringent mosaic texture, again similar to that shown by the *n*-tetradecyl monoester. The *n*-propyl, *n*-butyl, and *n*-hexyl monoesters showed a mosaic with somewhat different shapes to the mosaic domains, but with other textural details in accord with those observed for the *n*-pentyl monoester.

Although in Figure 1 we have included as S_{III} certain phases shown by the *n*-heptyl though *n*-nonyl monoesters, the identification must be regarded as speculative. Stable textures were obtained only after days at constant temperature. It was difficult to determine the exact onset of liquid crystallinity on raising the temperature of a crystalline sample, due to the very high viscosity of the lowest temperature mesophase. Spontaneous, but extremely slow flow was first observed in a sample of the *n*-octyl monoester above 100°C, and in the *n*-heptyl near 90°C. On vigorous maceration of a crystalline sample covered with a cover slip, plastic deformation of the *n*-octyl monoester could be observed at about 70°C. We believe that the lowest temperature transition exhibited by the *n*-octyl monoester is a solid-to-solid transition. The texture exhibited by the *n*-heptyl monoester at about 103°C, by the *n*-octyl monoester at 88°C, and by the *n*-nonyl monoester at 95°C differ in appearance from that exhibited by other members in the region labelled S_{III}. We present photomicrographs for comparison.

Stable characteristic textures were not observed for the *n*-heptyl monoester from 107–121°C, for the *n*-octyl monoester from 100–117°C, or for the *n*-dodecyl monoester from 103–110°C, although subtle shifts in the birefringence colors were frequently observed on heating or cooling untreated crystals through these regions. Uniform preparations of the *n*-heptyl and *n*-octyl monoesters, if held at 100°C or 95°C, respectively, then formed homeotropic preparations if heated above 107°C or 100°C, respectively. The optical properties of the *n*-heptyl monoester from 107–121°C, of the *n*-octyl monoester from 100–117°C, and of the *n*-dodecyl monoester from 103–110°C did not permit identification of the mesophases in these regions.

Selected photomicrographs are exhibited below. Unless otherwise stated, preparations are uncovered and textures are isothermally stable. Photographic magnification is 150X.

A. (i)-(vii). Variations of the texture of S_{III}. (i) The *n*-propyl monoester at 183°C from diglyme. (ii) The *n*-hexyl monoester at 101°C from diglyme. (iii) The *n*-heptyl monoester at 100–107°C from THF/diglyme. (iv) The *n*-octyl monoester at 88°C from THF. (v) The *n*-nonyl monoester at 95°C from diglyme. (vi) The *n*-dodecyl monoester at 105°C from diglyme. (vii) The *n*-tetradecyl monoester at 105°C from diglyme.

B. The texture of S_{II}. The *n*-pentyl monoester at 186°C from diglyme.

C. The texture of S_I. The *n*-octyl monoester at 210°C from diglyme. Preparation is covered.

D. A texture observed for the *n*-undecyl monoester at 213°C, either on cooling from the isotropic liquid or by isothermal deposition from diglyme.

E. The texture of the *n*-octyl monoester at 105°C. Regions of homeotropy are observed.

F. An unstable texture formed by deposition of the *n*-pentyl monoester from diglyme at 140°C. This texture is slowly replaced by an intensely birefringent mosaic texture under isothermal conditions.

5 CONCLUSIONS

We synthesized fourteen homologous *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid, and examined the thermal transitions of these compounds by DSC and hot-stage polarized microscopy. We classified the observed mesophases according to the scheme presented in Figure 1, and identified several of these mesophases microscopically. The three principal smectic mesophases observed exhibit characteristics consistent with those of S_E, S_B, and S_C. The great range of stability observed for the mesophase identified as S_E suggests that the *n*-propyl to *n*-hexyl monoesters might be useful as miscibility standards.

The monoesters of biphenyl-4,4′-dicarboxylic acid form one of the few classes of mesogenic compounds known to include tetramorphic homologs. We observed additional transitions of the *n*-heptyl, *n*-octyl, and *n*-dodecyl monoesters to phases which we were unable to identify, but which may represent one or two additional stable mesophases. If these observations can be corroborated by other methods, then the homologous series may exhibit almost the full range of mesomorphism known to exist.

We presented values for the temperature range, the enthalpy, and the entropy of each transition, attaching a careful estimate of the percent uncertainty of the enthalpy. We found that a significant contribution to the variability of values obtained for the enthalpy came from a dependence of instrumental response on scan rate. Although we have not determined the cause of this dependence, we have demonstrated that scan rate is yet one more factor that may need to be considered in comparing the results of two calorimetric studies of a given compound.

Gray and co-workers[13,14] note that those homologs of 4′-*n*-alkoxybiphenyl-4-carboxylic acid with an even number of carbons in the alkyl chain exhibit

N-I transitions at temperatures along a smooth curve which lies higher than the smooth curve along which the transitions of the odd homologs lie. This same pattern of alternation, persisting in the *S-I* transition region, is seen for the monoesters of biphenyl-4,4′-dicarboxylic acid, but for this homologous series, the homologs with an odd number of alkyl carbons lie on the upper curve. The carbonyl carbon of the ester lengthens the chain extending from the ring, and influences the odd-even alternation pattern as if it were an additional methylene unit.

The *N-I* or *S-I* transition temperature of a homolog of 4′-alkoxybiphenyl-4-carboxylic acid is about 15°C greater than that of the corresponding monoester of biphenyl-4,4′-dicarboxylic acid. This is noteworthy, because a lowering of the *N-I* or S_C-*I* transition temperature is observed if a substituent is introduced into the 3′ position of 4′-alkoxybiphenyl-4-n-carboxylic acid.[15] The introduction of the large nitro group into the 3′ position additionally converts the mono- and dimorphic homologs of 4′-*n*-alkoxybiphenyl-4-carboxylic acid into polymesomorphs with *N*, S_A, S_C, and S_D modifications[16] due to increased lateral repulsion.[13] Possibly, then, the lower transition temperatures and polymesomorphism of the monoesters of biphenyl-4,4′-dicarboxylic acid is due to lateral repulsions from the carbonyl group.

Another comparison can be made with the intensively researched *p*-*n*-alkoxybenzoic acids, which exhibit a nematic phase if the number of carbons in the alkyl chain is less than seven, and a S_C and possibly also a nematic phase if the number of alkyl carbons exceeds six.[17] Herbert[18] conducted calorimetric studies of these compounds. The average S_C-*N*, S_C-*I*, and N-I transition enthalpies of the *p*-*n*-alkoxybenzoic acids are 0.86, 2.36, and 0.66 kcal/mole, respectively. The average values we obtained for the S_I-*N*, S_I-*I*, and *N-I* transition enthalpies of the monoesters of biphenyl-4,4′-dicarboxylic acid are 0.268, 3.01, and 2.52 kcal/mole respectively. So we remark that: a) the S_C-*N* enthalpies of transition of the former compounds are, on the average, greater than the S_I-*N* transitions of the latter compounds; b) the S_C-*I* enthalpies of transition of the former compounds are, on the average, smaller than those of the S_I-*I* transition of the latter compounds; and c) the *N-I* enthalpies of transition of the former compounds are *much* smaller than those of the corresponding transition of the latter compounds. One may therefore conjecture that the nematic phase of the monoesters of biphenyl-4,4′-dicarboxylic acid is strongly associated, and perhaps retains organizational features of the S_I phase. It should be noted in this context that the average *N-I* transition enthalpy of these compounds slightly exceeds that normally[19] observed.

Linear least squares analysis of Herbert's data affords the relationships $\Delta H = 0.836n + 0.586$ and $\Delta H = 0.821n + 1.79$ for those homologs above butyl with, respectively, an even or odd number of carbons, n, in the alkyl chain; ΔH is the total *K-I* enthalpy of fusion in kcal/mole. The correlation coefficients are 0.985 and 0.989, respectively. Herbert did not obtain values for the enthalpy of fusion of the methyl and ethyl homologs due to sublimation. We performed the linear least squares analysis on the homologs higher than *n*-butyl to permit comparison with the linear least squares analysis we conducted on the *n*-alkyl monoesters of biphenyl-4,4′-dicarboxylic acid. Comparison of the linear least squares equations suggests that the crystalline state of a given homologous *n*-alkyl monoester of biphenyl-4,4′-dicarboxylic acid is energetically more stable—relative to its liquid state—than is the corresponding *p*-*n*-alkoxybenzoic acid homolog relative to its liquid state. That the slope of the linear equation is greater for the homologs of *p*-*n*-alkoxybenzoic acid than for the *n*-alkyl monoesters of biphenyl-4,4′dicarboxylic acid indicates, however, that the relative stability enjoyed by the latter compounds increases less quickly with increasing alkyl chain length than that of the former compounds.

Acknowledgments

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