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Tetrahydroxy-*p*-benzoquinone Tetraesters, The Simplest Discotics

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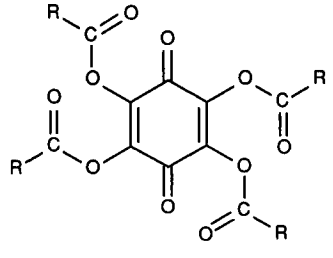
This report resolves uncertainty about mesomorphic behavior of tetrahydroxy-*p*-benzoquinone tetraesters. Both the tetraheptanoate and tetraoctanoate esters form stable mesophases over narrow temperature ranges. The phases are identified as columnar based upon their high viscosity and well-defined mosaic textures under a polarizing microscope. With only four flexible side chains attached to a one-ring rigid core, these appear to be the simplest discotics to exhibit columnar order.

Early in his pioneering work on discotic liquid crystals, Chandrasekhar reported discotic behavior by the tetraoctanoate ester of tetrahydroxy-*p*-benzoquinone, 1c.[1] The original report of an unstable discotic mesophase was subsequently withdrawn.[2] Owing to their simple structure and interesting core functionality the compounds appeared to merit reinvestigation. We report here details of our confirmation of discotic mesophase formation by the tetra-heptanoate and -octanoate esters, 1b and 1c. We have reported earlier on our study of 1c as thin, 20–80 Å, films on gold mirrors in which infrared analyses revealed apparent mesophase formation.[3]



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a R = pentyl
b R = hexyl
c R = heptyl

Experimental Section

Synthesis

Tetrahydroxy-*p*-benzoquinone[4] was esterified in one step[5] by reflux with ten equivalents of acid chloride under nitrogen followed by distillation of excess acid chloride.

Trituration of the brown residue gave crude tetraester. Successive recrystallization to constant transition temperatures from absolute methanol (1a and 1b) or from absolute ethanol (1c) under nitrogen gave pure tetraesters as pale yellow needles: *ca.* 30% yield for 1a and 1b and 55–60% yield for 1c. Like the tetraacetate,[6] these long chain esters are very sensitive to aqueous base. They are hydrolyzed to tetrahydroxy-*p*-benzoquinone on attempted thin-layer chromatography on silica gel. Owing to their sensitivity, HPLC on normal or reverse phase silica columns was unsuccessful. Structures were confirmed by infrared and ^{1}H and ^{13}C-NMR spectroscopy as well as C,H microanalysis.

Tetrahydroxy-p-*benzoquinone tetrahexanoate* (*1a*). Calculated for $C_{30}H_{44}O_{10}$: C, 63.81; H, 7.85. Found: C, 63.71; H, 7.71%. Infrared (KBr) 1785 (vs, ester C=O), 1700 (vs) and 1640 (s) cm^{-1} (quinone C=O and C=C). ^{1}H NMR ($CDCl_3$) δ (ppm), 0.90 (*t*, 12H, CH_3), 1.36 (*m*, 16H, CH_2's), 1.72 (*m*, 8H, β-CH_2), 2.56 (*t*, J = 7 Hz, 8 H, α-CH_2).

Tetrahydroxy-p-*benzoquinone tetraheptanoate* (*1b*). Calculated for $C_{34}H_{52}O_{10}$: C, 65.78; H, 8.44. Found: C, 65.53; H, 8.64%. Infrared (KBr) 1790 (vs, ester C=O), 1690 (vs) and 1650 (s) cm^{-1} (quinone C=O and C=C). ^{1}H NMR ($CDCl_3$) δ (ppm), 0.90 (*t*, 12 H, CH_3), 1.33 (*m*, 24 H, CH_2's), 1.72 (*m*, 8 H, β-CH_2-), 2.58 (*t*, 8 H, α-CH_2-). ^{13}C NMR ($CDCl_3$) δ (ppm), 14.0 CH_3, 22.4 C_3, 24.6 C_6, 28.5 C_4, 31.3 C_5, 33.5 C_2, 140.9 ring C, 169.2 ester C=O, 173.8 quinone C=O.

Tetrahydroxy-p-*benzoquinone tetraoctanoate* (*1c*). Calculated for $C_{38}H_{60}O_{10}$: C, 67.43; H, 8.93. Found: C, 67.40; H, 9.06%. Infrared (KBr) 1785 (vs, ester C=O), 1690 (vs) and 1650 cm^{-1} (s) (quinone C=O and C=C). ^{1}H NMR ($CDCl_3$) δ (ppm) 0.89 (*t*, 12 H, CH_3), 1.29 (*m*, 32 H, CH_2's), 1.72 (*m*, 8 H, β-CH_2-), 2.57 (*t*, 8 H, α-CH_2-). ^{13}C NMR ($CDCl_3$) δ (ppm) 14.0 CH_3, 22.6 C_3, 24.7 C_7, 28.8 C_4 and C_5, 31.6 C_6, 33.5 C_2, 140.9 ring C, 169.2 ester C=O, 173.8 quinone C=O.

Measurements

Infrared spectra were recorded using a Perkin-Elmer 1420 spectrophotometer; the 1601 cm^{-1} band of polystyrene was used to calibrate band frequencies. ^{1}H and ^{13}C NMR spectra were determined using Varian XL-200 and 300 spectrometers. Samples were deuteriochloroform solutions with tetramethylsilane as internal standard. Differential scanning calorimetry was performed using a Perkin-Elmer DSC-2 instrument. Samples of 1.25 to 3.62 mg were scanned at rates of 0.63 to 10°C/min; and temperatures and enthalpies were calibrated using an indium standard. Transition enthalpies were determined by cutting and weighing photocopies of the DSC traces in triplicate to establish relative peak areas. Optical textures and transition temperatures were determined using a Zeiss polarizing microscope equipped with a hot stage and Mettler model PC 6040 temperature programmer.

RESULTS AND DISCUSSION

Hexanoate ester 1a exhibited but one DSC transition between 25 and 100°C. However, the heptanoate and octanoate esters, 1b and 1c exhibited two, closely-spaced

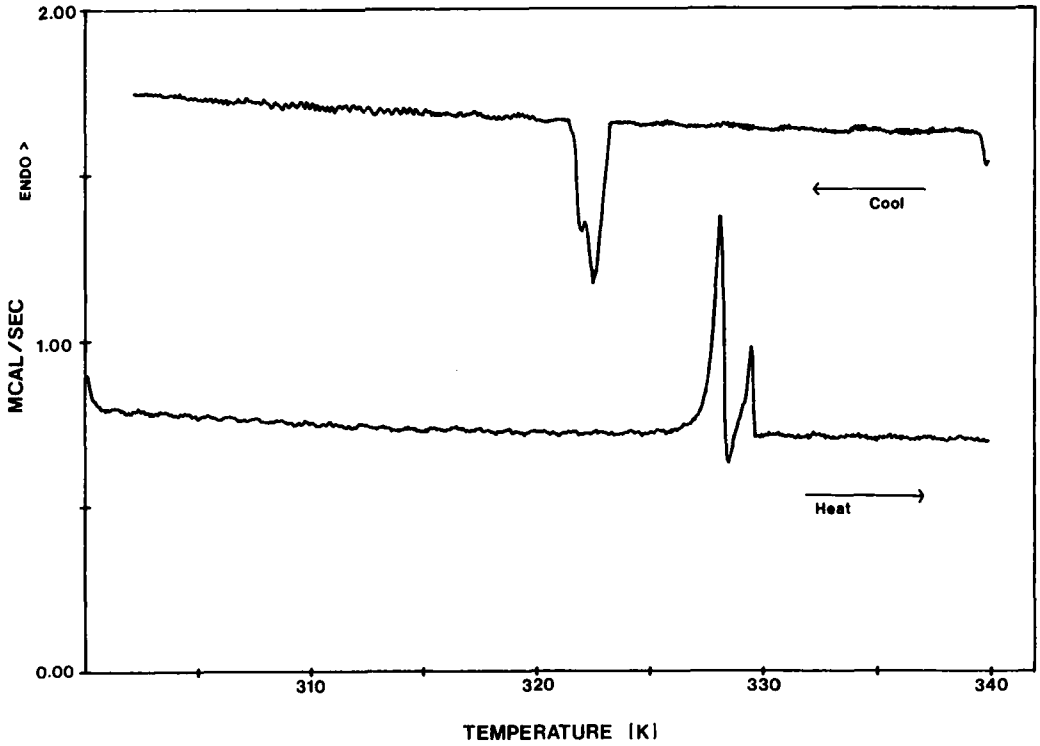

FIGURE 1 Differential Scanning Calorimetry traces for 1b heating rate 1.25°/min, cooling rate 1.25°C/min.

enantiotropic transitions, Figure 1 and Table. Thermal behavior on heating and cooling was reproducible over multiple cycles. Total enthalpy gain on heating and loss on cooling were equal and independent of heating or cooling rate. But the ratio $\Delta H_{K\rightarrow D}/\Delta H_{D\rightarrow I}$ increased modestly as the heating rate increased. A small

TABLE I

Phase Transition Temperatures and Enthalpies for Tetrahydroxy-*p*-benzoquinone Tetraesters.[a]

Compound	Method	T_f	ΔH_f[b]	$T_{K\rightarrow D}$	$\Delta H_{K\rightarrow D}$	$T_{D\rightarrow I}$	$\Delta H_{D\rightarrow I}$
1a	DSC	55	11.1				
	M[c]	54					
1b	DSC			55	5.9	57	1.7
	M[c]			55		58	
1c	DSC			68[e]	2.8	70	8.0
	M[c]			67		69	
	IR[d]			~57		~59	

[a]Temperature in °C, $\underline{\Delta H}$ in cal/g.
[b]Precision ± 10%, heating rate 1.25°C/min.
[c]Optical polarizing microscopy.
[d]For 20–80 Å films on gold surfaces using infrared detection.
[e]A melting point at 64°C was reported in reference 5.

exotherm just to the high temperature side of the low temperature endotherm was observed on heating. Its area decreased with heating rate and virtually disappeared at a rate of 0.63°C/min. We attribute this to conversion of some metastable material to the mesophase. Slow heating has the effect of annealing the sample.

Optical microscopy confirmed the liquid crystalline nature of the phases formed by 1b and 1c between the temperatures of their DSC endotherms. Crystals of 1b and 1c are transformed to viscous fluids which exhibit well-defined mosaic textures with homeotropic regions when viewed between crossed polars, Figure 2.[7] The mosaic texture strongly suggests columnar order of these disc-like mesogens.[8] Definitive evidence awaits X-ray diffraction experiments. The mesophases of 1b and c appear to be stable indefinitely at 57° and 68° respectively.

Thus, Chandrasekhar et al.'s original report of discotic behavior by 1c[1] is verified and that of its heptanoate homolog 1b described for the first time. Comparison of the transition temperatures we report here for bulk samples of 1c to those we detected in 20 to 80 Å films on gold surfaces using infrared spectroscopy[3] reveal a ten degree perturbation of transition temperatures, the thin films disordering at lower temperatures (Table). The infrared study revealed that the lower transition is associated with side-chain disordering while the upper transition involves disordering of quinone cores by movement out of coplanarity with the gold surface. Detailed studies of bulk phase discotics using infrared and NMR spectroscopy have revealed analogous changes at phase transitions.[9] At $T_{K\rightarrow D}$ sidechains disorder,

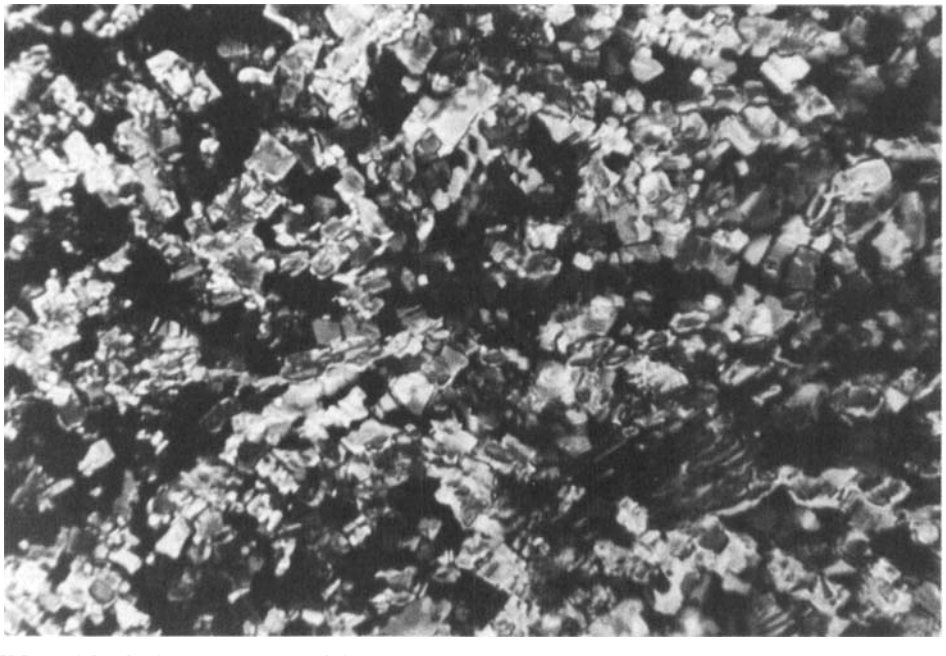

FIGURE 2 Optical Micrograph of the Mesophase 1c Between Crossed Polars at 68°C, magnification X200.

while at $T_{D\rightarrow I}$, cores unstack. Thus, the available evidence strongly supports discotic mesophase formation in thin films of 1c.

While other discotics with single ring cores[10] or with only four side-chains[11] are known, the tetrahydroxy-*p*-benzoquinone tetraesters 1b and 1c are the only examples which share both these features. Mesogens with one-ring cores and three side-chains give only nematic discotic, N_D, phases.[12] Thus, 1b and 1c are the simplest known discotics to exhibit columnar order.

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