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Effect of Heteroatoms in the Side Chains of Disklike Molecules on the Formation of Discotic Liquid Crystalline Phases

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Incorportion of oxygen and sulfur atoms into the side chains of discotic liquid crystals generally results in a depression of both the crystal to discotic and discotic to isotropic transition temperatures relative to the *n*-alkyl analogue. In contrast, replacement of the methylenes in side-chain positions 4 of 2,3,6,7,10,11-hexakis(alkanoyloxy)triphenylenes increases the clearing (M–I) temperature from 120 to 200 °C. This effect is specific for sulfur substitution, to the triphenylene series, and to the 4-position. It is not expected, based on a simple model for discotic-phase formation.

Introduction

Rodlike[1] and disklike[2] mesogens consist of a rigid core and flexible aliphatic chains. Although many series of cores have been studied in both cases, very little is known about the effect of aliphatic chain structure on the formation of mesophases.[3,4] In an effort to develop structure–property relationships for discotic liquid crystals we have undertaken an investigation into the effect of variation side-chain structure on the thermal-phase behavior of disklike molecules.

Discogens consist of a flat rigid core from which radiate flexible aliphatic side chains. The mesophase formed by disklike molecules consists of columns of molecules which in turn form a two-dimensional array. From various spectroscopic[5] and scattering[6a] techniques, it is known that in the crystal (K) phase, the side chains are relatively ordered and that in the mesophase (M) they are substantially disordered. A simple model for discotic behavior involves a K–D transition caused by side-chain conformational disordering ("melting") followed by clearing caused by unstacking of cores at a higher temperature.[4a,6] Thus, side-chain variation should affect only the K–M transition. However, incorporation of oxygen into the side chains of hexakis(alkanoyloxy)benzenes has an effect on both the K–M and the M–I transitions.[4b] This effect varies with position in the side chain, and no clear pattern emerges from the data reported by Tabushi et al.[4b]

We report on the effect of oxygen and sulfur incorporation in the side chains of three series of disklike molecules: the hexaesters of benzene-, 1,2,3,4,5,6-*all-trans*-cyclohexane-, and 2,3,6,7,10,11-triphenylenehexa(alcohol)s.

Results and Discussion

The thermal-phase behavior of disklike molecules with heteroatom-containing side chains is shown in Table I. Both crystal to mesophase and mesophase to isotropic transitions are affected by replacement of methylene groups by heteroatoms. The effect is highly dependent on the position of the heteroatom, but in a less regular way than that of methyl branching described previously.[4a,6b] With few exceptions both transition temperatures are depressed relative to the *n*-alkyl analogues. Generally, the enthalpy change at the clearing transition is lowered upon incorporation of heteroatoms into the side chains. The effects on the thermal-phase behavior of the benzene and cyclohexane series of specific side chains are similar; the effects in the triphenylene series are different.

Table I. Thermal-Phase Behavior of Disklike Molecules with Heteroatom-Containing and *n*-Alkyl Side Chains[a]

core	side chain	transition	T	ΔH	ΔS
benzene	C8[b]	K–M	80.2	10.9	30.9
		M–I	83.3	4.1	11.5
benzene	C8(3-thia)[c]	K–I	69	11.8	34.5
benzene	C8(4–thia)	K–I	101	14.7	39.2
benzene	C8(5-thia)	K–?	52.1		
		?–M	52.8	7.0[d]	
		M–I	56.7	3.7	11.1
benzene	C8(7-thia)	K–M	31.5	8.4	27.7
		M–I	37.4	1.2	3.9
cyclohexane	C8[e]	K–M	76	14.7	42.2
		M–I	199	2.7	5.7
cyclohexane	C8(4-oxa)	K–M	47	15.7	49.1
		M–I	87	0.3	0.9
cyclohexane	C8(7-oxa)	K–M	44	11.3	35.7
		M–I	144	1.6	3.9
cyclohexane	C8(3-thia)	K–M	57	10.1	30.6
		M–I	106	0.8	2.2
cyclohexane	C8(4-thia)	K–M	86	7.5	20.8
		M–I	183	1.6	3.4
cyclohexane	C8(5-thia)	K–M	64	6.0	17.8
		M–I	189	1.7	3.7
cyclohexane	C8(7-thia)	K–M	56	21.5	65.5
		M–I	172	1.8	4.0
triphenylene	C7[f]	K–M	108	3.4	8.9
		M–I	118	0.5	1.2
triphenylene	C7(4-thia)	K–M	86	3.7	10.2
		M–I	198	1.6	3.5
triphenylene	C8[f]	K–M	66	7.5	22.1
		M–I	129	0.5	1.4
triphenylene	C8(4-oxa)	K–I	94	6.3	17.2
triphenylene	C8(3-thia)	K–K	69	1.4	4.2
		K–M	75	2.7	7.8
		M–I	138	1.1	2.7
triphenylene	C8(4-thia)	K–M	57	6.4	19.3
		M–I	202	1.6	3.3
triphenylene	C8(5-thia)	K–I	98	5.1	13.6
triphenylene	C9[f]	K–M	65	5.6	16.4
		M–I	125	0.5	1.2
triphenylene	C9(4-thia)	M at 25 °C			
		M–I	203	1.0	2.1

[a] K, crystal; M, mesophase; I, isotropic; ?, phase structure not determined. Temperatures in °C; ΔH in kcal mol^{-1}; ΔS in cal K^{-1} mol^{-1} from DSC. [b] Compare to data in ref 2b. [c] Lit.[4b]: K 67 M 68 I. [d] Sum of ΔH for two transitions. [e] Compare to data in ref 12c. [f] Compare to data in ref 12b.

Depression of K–M transition temperature by incorporation of heteroatoms in the side chain of disklike molecules is reasonable based on the model for separate disordering temperatures of side chains and cores of disco-

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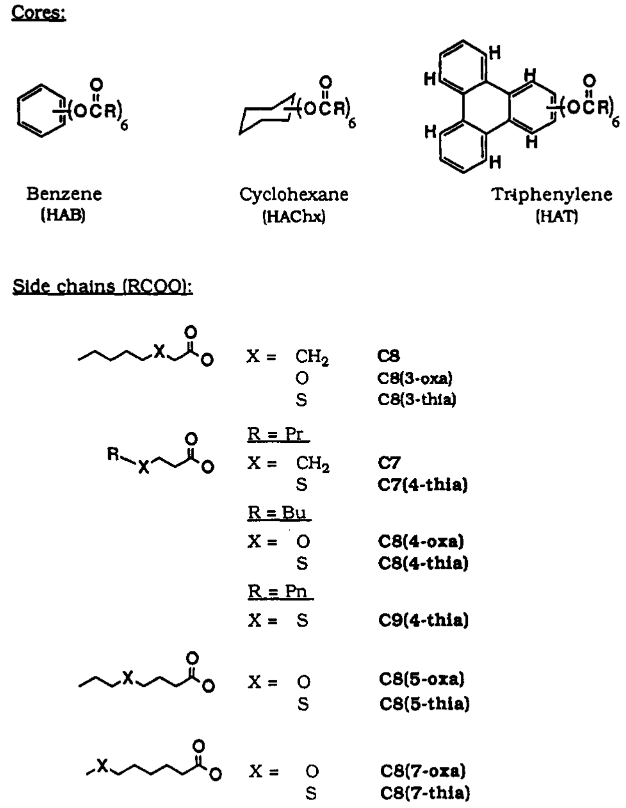
Chart I



gens. Changes in side-chain structure are expected to affect the K–M transition temperature, and the depression might be explained in terms of the lower rotation barriers around a carbon–heteroatom bond relative to a carbon–carbon bond.[7] The depression of clearing-point temperature upon changing the side-chain structure is not predicted by this model. We have recently described the effect of bromine substitution on the side chains of discogens in terms of dipole–dipole interactions between the side chains and the polar cores in the mesophase and the isotropic state.[8] A depression in the clearing point of ω-bromine substituted discotics was explained as arising from stabilization of the isotropic phase by dipole–dipole interactions between the side-chain terminal C–Br bond and the ester linkage of the core, which are not possible in the columnar mesophase. Such dipolar interactions might explain the effects of heteroatom incorporation reported here.

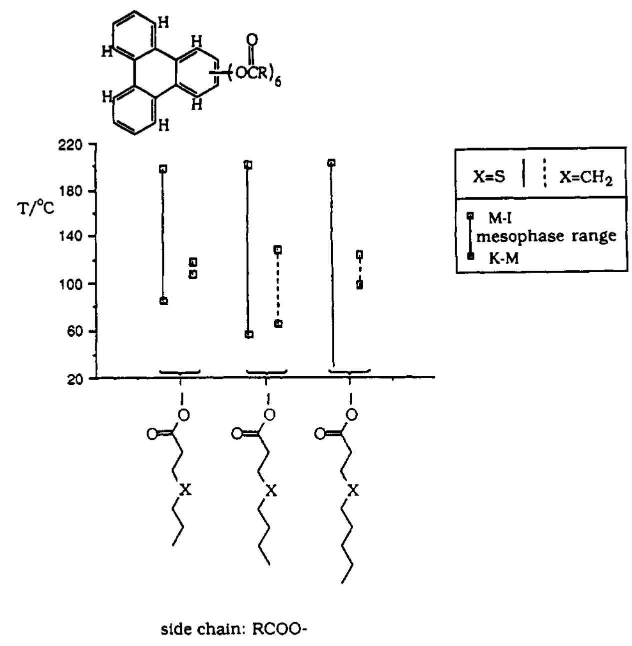


Figure 1. Thermal-phase behavior of ((3-(alkylthio)propanoyl)oxy)triphenylene and the corresponding (*n*-alkanoyloxy)triphenylene. (Compare data for *n*-alkyl side chain to those in ref 12c.)

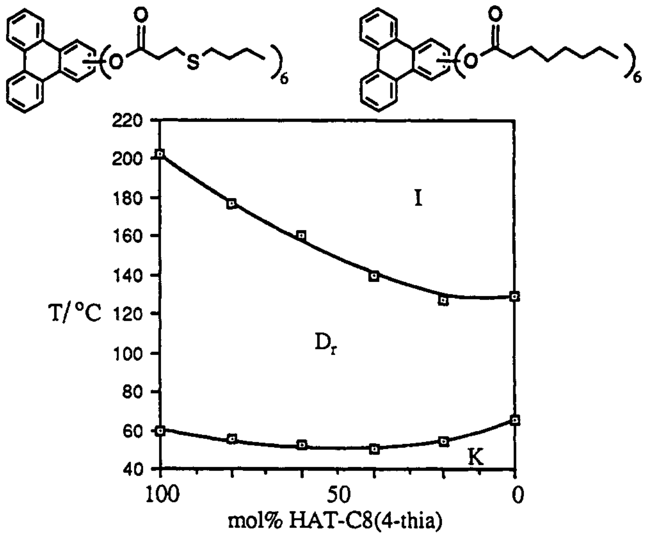


Figure 2. Phase diagram for mixtures of ((3-(butylthio)propanoyl)oxy)triphenylene and (octanoyloxy)triphenylene.

The most interesting feature of these data is the high clearing temperatures exhibited by the enantiotropic mesophases formed by (3-(alkylthio)propanoyl)oxy, e.g., C8(4-thia), members of the triphenylene series (ca. 200 °C), relative to those of the related *n*-alkyl compounds (ca. 120 °C). This stabilization of the mesophase is specific to sulfur in the 4-position of the triphenylene series. Increasing the side chain length in the triphenylene 4-thia ester derivatives depresses the K–M transition temperature without affecting the clearing temperature (Figure 1). The enthalpy change for the clearing transition is higher than that for the *n*-alkyl analogues. On the benzene core the C8(4-thia) side chain results in a high melting point (relative to the *n*-octanoate clearing point), and on the cyclohexane core a small depression in the clearing temperature is observed. We have previously shown that variation of side-chain structure does not affect the molecular packing in the mesophase. A phase diagram for mixtures of the C8 and C8(4-thia) members of the tri-

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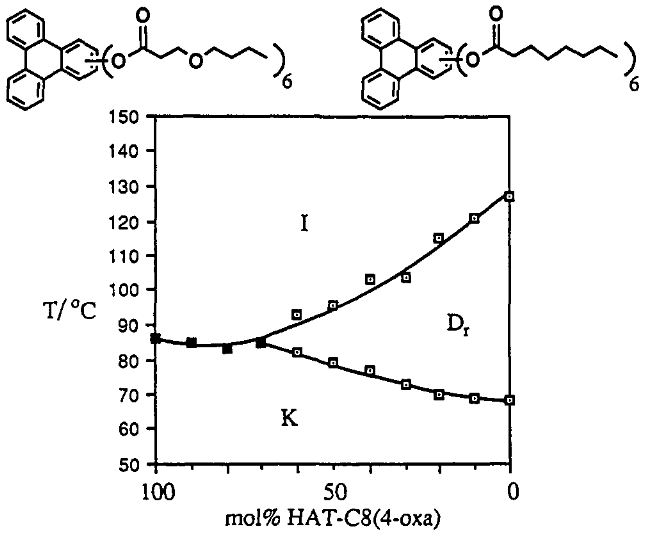

Figure 3. Phase diagram for mixtures of ((3-(butyloxy)-propanoyl)oxy)triphenylene and (octanoyloxy)triphenylene.

phenylene series (Figure 2) indicates that the two components form mesophases of the same structure, and X-ray diffraction of the two compounds is similar. The mesophase of the *n*-octanoyloxy analogue (as determined by X-ray diffraction) has been described as a $P2_1/a$ rectangular structure.[9] However, in this study the hydrocarbon analogue gave rise to only four Bragg diffractions. An intense diffraction at 19.1 Å indicates high short-range order, and the weak diffraction at 69.8 Å indicates some longer range order which might be interpreted as arising from a D_r, $P2_1/a$ phase. Diffuse bands at 14.6 and 4.6 Å, presumably from intercolumnar and intracolumnar spacings, respectively, account for the remaining diffractions. Similar low-angle diffraction bands are present in the X-ray pattern of the 4-thia analogue, with slightly larger distances (21.8, 73.8 Å). The additional diffuse bands appear at 4.7 and 3.5 Å for the sulfur analogue. The optical textures of the C8(4-thia) and C8 compounds are not identical, but both indicate the presence of a discotic or smectic mesophase. The mesophase structure formed by these two analogues obviously resemble each other; thus, the increased clearing temperature of the thia analogue is not the result of large changes in molecular packing in the mesophase.

Whereas the 4-thia analogue of HAT-C8 forms a particularly stable mesophase, the 4-oxa analogue melts at 94 °C, a temperature above the K–M transition of the *n*-alkyl side-chain compound, but below the expected clearing temperature, ca. 120 °C. The transition curves of the phase diagram of mixtures of HAT-C8 and HAT-C8(4-oxa) (Figure 3) are linear, indicating an extremely good homology between the crystal packing of the two components. Extrapolation of the K–M transition curve to pure oxa analogue gives a virtual K–M transition temperature of ca. 68 °C. Incorporation of oxygen at the 4-position of the side chain of HAB-C8 and HAChx-C8 depresses both the K–M and M–I transition temperatures.

Increased stability of the mesophase by incorporation of sulfur at the 4-position in the triphenylene series might be due to an increase in the attraction between stacked cores along the column axis. This could arise from intermolecular sulfur–sulfur interactions along the axis or from intramolecular sulfur–sulfur interactions which increase the rigidity of the side chains and increase the effective size of the core. An experimentally observable consequence should be a high degree of conformational order in the mesophase about the bonds from C$_1$ to sulfur at the 4 position relative to the essentially liquid side chains of *n*-alkyl analogues. These observations pose a challenge to seekers of a comprehensive theory of structure–property relationships for discotics.

Experimental Section

Hexahydroxybenzene,[10a] 1,2,3,4,5,6-*all-trans*-hexahydroxycyclohexane (*scyllo*-inositol),[10b] and 2,3,6,7,10,11-hexahydroxytriphenylene[10c] and (pentylthio)acetic,[11a] 3-(alkylthio)propanoic,[11b] 3-(propyloxy)butanoic,[12a] 4-(propylthio)butanoic,[11c] 6-(methoxy)hexanoic,[12b] and 6-(methylthio)hexanoic[11d] acids were prepared according to variations of literature methods. Acyl chlorides were prepared by reaction between the carboxylic acid and oxalyl chloride at room temperature. Acylation of hexahydroxybenzene[13a] and -triphenylene[13b] were carried out at 140 °C in the absence of solvent for 3–4 h using an excess of the side-chain acyl chloride. Inositol was acylated in trifluoroacetic acid at room temperature for 18 h.[13c] Disklike compounds were purified by flash chromatography on silica gel[14] followed by repeated recrystallization from aqueous ethanol to constant phase transition temperatures and gave satisfactory infrared, ^{1}H NMR, chromatographic, and combustion analyses. The thermal-phase behavior was studied by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-4 instrument. All thermal transitions were reproducible during repeated heating and cooling cycles. X-Ray diffraction ($\lambda = 1.542$ Å) was performed on unoriented samples in thin-walled quartz tubes (Mark-Rohrchen, FRG, from Charles Supper Co., Natick, MA) on a Seimens Kristalloflex Statton flat-film camera equipped with a brass block heating unit. Optical microscopy was performed on an Olympus B-2 microscope equipped with a Thomas (Philadelphia, PA) hot stage and an Omega microprocessor controller and digital reporting thermocouple. Mixtures of disklike molecules were prepared by freeze-drying benzene solutions of two components.

Supplementary Material Available: ^{1}H NMR and IR spectra and combustion analysis data for all new disklike compounds (5 pages). Ordering information is given on any current masthead page.

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