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Control of Thermal Phase Behavior of Disklike Molecules by Modification of Side-Chain Structure[†]

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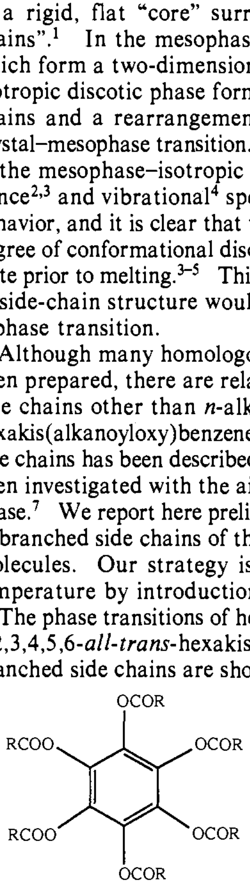
Abstract: Introduction of branch points into the side chains of hexakis(alkanoyloxy)benzenes and 1,2,3,4,5,6-*all-trans*-hexakis(alkanoyloxy)cyclohexanes widens the temperature range over which the columnar mesophase is stable primarily by lowering the cyrstal–discotic transition temperature.

Discotic mesophases are formed by disklike molecules consisting of a rigid, flat "core" surrounded by flexible aliphatic "side chains".[1] In the mesophase these molecules stack in columns which form a two-dimensional array. A simple model for thermotropic discotic phase formation involves a melting of the side chains and a rearrangement of the cores into columns at the crystal–mesophase transition. Unstacking on the cores takes place at the mesophase–isotropic transition. Nuclear magnetic resonance[2,3] and vibrational[4] spectroscopy provide evidence for this behavior, and it is clear that the side chains already exhibit a high degree of conformational disorder at their ends even in the crystal state prior to melting.[3-5] This simple model predicts that variation of side-chain structure would effect principally the crystal–mesophase transition.

Although many homologous series of disklike molecules have been prepared, there are relatively few reports of discogens with side chains other than *n*-alkyl. The thermal phase behavior of hexakis(alkanoyloxy)benzenes with sulfur- and oxygen-containing side chains has been described.[6] Chiral branched side chains have been investigated with the aim of inducing a twist to the discotic phase.[7] We report here preliminary results of a study of the effect of branched side chains of the thermal phase behavior of disklike molecules. Our strategy is to depress the side-chain melting temperature by introduction of branch points.

The phase transitions of hexakis(alkanoyloxy)benzenes (**1**) and 1,2,3,4,5,6-*all-trans*-hexakis(alkanoyloxy)cyclohexanes (**2**) with branched side chains are shown in Table I.[8] All mesophases are viscous, and highly birefringent, displaying mosaic textures. The mesophase–crystal transitions display supercooling whereas the isotropic–mesophase transitions do not. Phase diagrams for mixtures of (methyloctanoyl)oxy and the *n*-octanoyloxy side chain discogens display stable mesophases across the entire composition range. In analogy to the work of Sackmann on the classification of smectic mesophases,[11] this indicates that the type of mesophase formed is unaffected by branching in the side chain of discogens.



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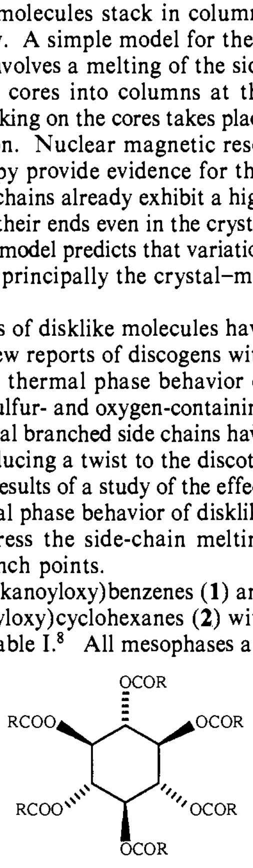

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The results given in the table show that the thermal phase behavior of disklike molecules can be controlled by variation of the side-chain structure. The position of branching affects the transition temperatures. Methyl branches in the 2-position of the octanoyloxy chain results in a destabilization of the columnar phases. In contrast, branching in the middle of the chain results in a depression of the crystal–mesophase transition without greatly affecting the mesophase–isotropic transition temperature. This has the effect of widening the temperature range over which the mesophase is thermodynamically stable. Branching at C-7 of the octanoate chain has little effect.

Table I. Thermal Phase Transitions of Disklike Compounds[a]

side chain: RCOO	benzene core	cyclohexane core
hexanoyloxy	K_1 77 K_2 95 I[b]	K 68.5 M 199.5 I[c]
heptanoyloxy	K 81 M 86 I[b]	K 68.0 M 200.0 I[c]
octanoyloxy	K 82 M 84 I[b]	K 76 M 199 I[d]
nonanoyloxy	K 81 I (I 75 M)[e,b]	K 78 M 194 I[d]
(2-methyloctanoyl)oxy	I at 20 °C	K 42 M 116 I
(3-methyloctanoyl)oxy	K 96 I	K 48 M 195 I
(4-methyloctanoyl)oxy	M 96 I[f]	M 181 I[f]
(5-methyloctanoyl)oxy	M 102 I[f]	M 186 I[f]
(6-methyloctanoyl)oxy	K 61 M 87 I	K 54 M 197 I
(7-methyloctanoyl)oxy	K_1 81 K_2 85 M 87 I	K 87 M 201 I
(6-ethyloctanoyl)oxy	K 60 M_1 86 M_2 87 I	K 38 M 186 I
(5-cyclopentylpentanoyl)oxy	K 130 I	K 139 M 199 I
(5-methylheptanoyl)oxy	K_1 82 K_2 96 K_3 107	K 68 M 196 I
(7-methylnonanoyl)oxy	K 52 M 75 I	K 44 M 192 I

[a] Temperatures from DSC in °C. K, crystal; M, mesophase; I, isotropic. [b] Compare to literature values in ref 9. [c] Literature values from ref 10. [d] Compare to literature values from ref 10. [e] Monotropic transition in parentheses. [f] The mesophase is stable at room temperature. T_{K-M} has not been determined.

As a result of side chain melting point depression by branching, the 7-methyl analog displays an enantiotropic mesophase, whereas hexakis(nonanolyloxy)benzene shows only a monotropic mesophase. Since this effect could be caused by the stereoheterogeneity of the sample, discogens with 6-(ethyloctanoyl)oxy side chains were prepared. These stereohomogeneous samples also displayed lower crystal–mesophase transitions than the *n*-alkanoyloxy analogues. The 5-(cyclopentylpentanoyl)oxy side chain is of particular interest. In the case of this side chain with a benzene core a high melting point is obtained whereas a particularly high crystal-mesophase transition is found for the cyclohexane core.

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[†] Dedicated to Prof. E. J. Corey on the occasion of his 60th birthday.

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(8) All compounds were prepared according to literature methods[9,10] and gave satisfactory ^{1}H NMR, IR, and elemental analyses. Transition temperatures were determined on a Perkin-Elmer DSC-4 and confirmed by optical microscopy between crossed polarizers.

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We believe that this is due to a high-chain "melting" temperature. The side chains melt at a temperature above that necessary to cause columns consisting of benzene cores to unstack. However, cyclohexane cores unstack at a higher temperature, so a mesophase is observed with this core.

The enthaply change for the crystal–mesophase transition of the branched compounds is lower than that for the *n*-alkanoyloxy compounds. As predicted by this model, the enthalpy change for the mesophase–isotropic transition is not reduced by branching.

These observations can be explained by the following arguments. Branches close to the core at C-2 interfere sterically with efficient stacking. Stacked benzene cores in the discotic phase are separated by an average distance of 4.6 Å.[9] The depression of melting point by branching in the middle of the side chains might be due to steric crowding with neighboring chains, and an increase in the conformational disorder about the branch. Branching at C-7 of the octanoate chain has little effect because at this distance from the cores the chains are not crowded by their neighbors and the region of the branch point is already disordered to a high degree prior to melting of the crystal phase (vida supra).

These data fit the model of separate side chain "melting" points and core "unstacking" temperatures for discotic liquid crystals. By varying the side-chain structure of discogens we are able to control the temperature range over which the discotic phase is stable. Work is in progress to further control the mesophase range of disklike molecules.

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Supplementary Material Available: ΔH and ΔS values for thermal transitions of all compounds (2 pages). Ordering information is given on any current masthead page.

Reduction of Azoalkanes by Benzhydryl Radicals

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Abstract: Benzhydryl radicals donate a hydrogen atom rapidly to the less hindered nitrogen atom of aliphatic and aromatic azo compounds, leading to the corresponding hydrazines. When the initially formed hydrazyl radical possesses a weak β-bond, it undergoes scission before receiving a second hydrogen atom. Thermolysis of benzpinacol with azocyclopropane causes a complex rearrangement to 1,5-diazaoct-5-en-1-yne (**21**).

Attempted triplet sensitization by aromatic ketones in the presence of a hydrogen donor can lead to complications due to the participation of ketyl radicals, a phenomenon commonly called chemical sensitization.[1] Recently, it was discovered in this laboratory that irradiation of xanthone with azocyclopropane (ACP) and thiophenol afforded propanal cyclopropylhydrazone (**6**) and propanal azine (**7**).[2] The mechanism in Scheme **I**, involving hydrogen transfer from xanthydryl radical (**1**) to the ground-state azo linkage, was proposed to explain the formation of these products (s = syn, a = anti).

Although the reducing properties of hydroxyalkyl radicals are well known[3-6] and the azo linkage is readily attacked by radicals,[7] the only azo compounds reported to react with ketyl radicals are azo dyes.[8-11] In order to test the above mechanism, we studied the reduction of azoalkanes by thermally generated benzhydryl radicals.[12]

I. Results

The photoreaction of benzophenone with triethylamine produces a near quantitative yield of benzhydryl radical,[13] but irradiation of this solution in the presence of ACP caused rapid destruction of starting azoalkane and formation of a complex mixture. In contrast, azo-*tert*-butane (ATB) was reduced to 1,2-di-*tert*-butylhydrazine (**8**) under the same conditions. To confirm the participation of the benzhydryl radical, this species was produced independently in the presence of ATB by thermolysis of benzpinacol,[14] leading cleanly to **8**. Further investigation of the thermal reaction using the azoalkanes listed in Table I showed reduction to be general.

All of the aliphatic hydrazines were identified by comparing their ^{1}H and/or ^{13}C NMR spectra (cf. Table II) with those from the literature[15] or from authentic samples made by catalytic hydrogenation[16] of the corresponding azoalkane. The structures of the arylhydrazines are supported by the similarity of their ^{13}C chemical shifts to those of hydrazobenzene. Products **21**, **25**, **27**, and **29** were identified by comparison with independently synthesized samples.[17] The reduction products of **36** were confirmed by NMR comparison with a mixture of acetone azine and acetic acid.

Thermolysis of benzpinacol proceeds at low enough temperature (130 °C) that competing decomposition of the azoalkanes selected

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