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Structure–Property Relationships for the Thermal Phase Behavior of Discotic Liquid Crystals: The Effect of Branching and Unsaturation in the Side Chains of Disklike Molecules

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Abstract: The crystal-to-discotic liquid–crystalline phase transition associated with disklike molecules can be explained in terms of a disordering of the side chains. Unstacking of the columnar arrangement takes place at the clearing transition. Introduction of branch points into the side chains of hexakis(alkanoyloxy)benzenes and 1,2,3,4,5,6-all-trans-substituted cyclohexanes widens the temperature range over which the columnar mesophase is stable primarily by lowering the crystal–discotic transition temperature. Maximum depression of this transition occurs when this branch point resides near the middle of the side chain. The effect of unsaturation in the middle of the side chains is to increase the disordering temperature. If the side chain remains ordered up to the temperature at which the cores unstack, no mesophase is observed.

Introduction

Although it is difficult to predict the formation of liquid–crystalline phases ("mesophases") with any certainty, for 100 years chemists have been interested in developing structure–property relationships for these intriging molecules.[1] More recently the application of rodlike liquid crystals in technological devices[2] has demanded tailoring of thermal phase properties of mesogens. Although there are reports of many homologous series of rodlike mesogens,[1] very little is known about the variation of the flexible chain units of these molecules.[3] More recently[4] liquid crystal formation by disklike molecules (discogens)[5] has been described. The mesophase formed by these disks consists of columns of molecules. Within a column the molecules can be either periodically or aperiodically arranged. These columns in turn form two-dimensional crystallike arrays (i.e. hexagonal, rectangular, oblique).[5] All discogens reported to date consist of a flat, rigid core, surrounded by a flexible aliphatic fringe of side chains. We have been particularly interested in the effect of side-chain structure of disklike molecules which form discotic liquid–crystalline phases.[6,7] There have been very few reports of side chains other than n-alkyl.[6,8]

A simple model, Figure 1, for discotic phase formation involves separate disordering temperatures for the side chains and the cores. The crystal (K) phase consists of a three-dimensional array of mesogens with high positional and orientational order. Upon heating, at the crystal-to-discotic (D) phase transition the side chains undergo disordering but the cores remain stacked in columns. Only at the discotic-to-isotropic (I) or clearing transition

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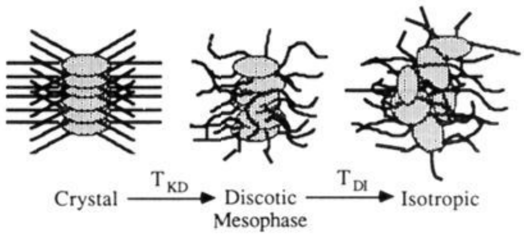

Figure 1. A simple model for discotic phase behavior. In the crystalline phase there is a high degree of positional and orientational order to the cores, and the side chains have a high degree of conformational order. In the discotic phase, the side-chain conformational order is lost; orientational order and some of the positional order of the cores are maintained. In the isotropic phase all order is lost.

Table I. Thermal-Phase Behavior of Hexakis(alkanoyloxy)benzenes with *n*-Alkyl and Branched Side Chains[a]

	transition	T	ΔH	ΔS
HAB-C5[b]	K–I	103		
HAB-C5(3-Me)	K–I	154	16.5	38.7
HAB-C5(4-Me)	K–I	148	14.8	35.0
HAB-C5(5-cyPn)	K–I	130	14.7	36.4
HAB-C7[c]	K–D	80.3	10.9	30.8
	D–I	85.7	7.2	20.1
HAB-C7(4-Me)	K–I	107	7.0	18.4
HAB–C7(5-Me)	K–K	82	1.8	5.2
	K–K	98	0.5	1.4
	K–I	108	5.6	14.8
HAB-C8[c]	K–D	80.2	10.9	30.9
	D–I	83.3	4.1	11.5
HAB-C8(2-Me)	I at 25 °C			
HAB-C8(3-Me)	K–I	96	8.6	23.3
HAB-C8(4-Me)	D at 25 °C			
	D–I	96	7.4	20.1
HAB-C8(5-Me)	D at 25 °C			
	D–I	102	3.7	9.8
HAB-C8(6-Me)	K–D	61	4.0	2.1
	D–I	87	3.6	10.1
HAB-C8(7-Me)	K–K	81.6	1.4	3.8
	K–D	85.0	2.9	8.1
	D–I	86.9	4.9	13.6
HAB-C8(3,7-diMe)	K–I	94	10.1	27.6
HAB-C8(6-Et)	K–D	60	6.0	18.1
	M–M	86		
	D–I	87	$\sum\Delta H = 4.2$[d]	
HAB-C9[c]	K–I	81	16.6	46.9
	(I–D	74.8	2.6)	
	(D–K	73.0	12.1)	
HAB-C9(4-Me)	D at 25 °C			
	D–I	84	5.2	14.6
HAB-C9(7-Me)	K–D	52	4.3	13.1
	D–D	74	0.1	0.4
	D–I	75	3.1	8.9

[a] K, crystal; M, mesophase; I, isotropic. Temperatures in °C, ΔH in kcal mol^{-1}, ΔS in cal mol^{-1} K^{-1} from DSC. Monotropic transitions in brackets. [b] From ref 10. [c] Compare to ref 11. [d] Sum of ΔH for two transitions.

Table II. Thermal-Phase Behavior of 1,2,3,4,5,6-*all-trans*-Hexakis(alkanoyloxy)cyclohexanes with *n*-Alkyl and Branched Side Chains[a]

	transition	T	ΔH	ΔS
HAChx-C5[b]	K–I	207.5		
HAChx-C5(5-cyPn)	K–K	139	1.4	3.4
	K–D	143	6.5	15.6
	D–I	200	1.9	4.0
HAChx-C6[c]	K–D	68.5	5.0	14.7
	D–I	199.5	2.1	4.5
HAChx-C6(4-Me)	K–I	209	6.5	13.5
HAChx-C7[d]	K–D	69	13.8	40.3
	D–I	201	3.3	7.0
HAChx-C7(5-Me)	K–D	68	5.1	14.9
	D–I	196	3.8	8.0
HAChx-C8[d]	K–D	76	14.7	42.2
	D–I	199	2.7	5.7
HAChx-C8(2-Me)	K–D	42	4.2	13.4
	D–I	116	2.4	6.1
HAChx-C8(3-Me)	K–D	49	5.9	18.2
	D–I	195	3.9	8.3
HAChx-C8(4-Me)	D at 25 °C			
	D–I	181	2.7	6.0
HAChx-C8(5-Me)	D at 25 °C			
	D–I	187	2.4	5.2
HAChx-C8(6-Me)	K–D	54	4.1	12.7
	D–I	197	2.1	4.6
HAChx-C8(7-Me)	K–D	87	7.5	20.9
	D–I	201	2.2	4.6
HAChx-C8(3,7-diMe)	K–D	71	2.5	7.1
	D–I	185	3.7	8.0
HAChx-C8(6-Et)	K–D	38	1.5	4.8
	D–I	186	2.1	4.6
HAChx-C9[d]	K–D	78	12.6	35.9
	D–I	195	1.9	4.1
HAChx-C9(7-Me)	K–D	44	5.2	16.3
	D–I	192	2.1	4.6

[a] See Table I for explanation of table. [b] From ref 13. [c] From ref 12. [d] Compare to ref 13.

do the cores unstack. The liquidlike nature of side chains in columnar discotics and the uncoupling of core and side-chain disordering are implicit in the results of several groups[7,9] and have been clearly stated by Heiney et al.[10] and by us.[6,11] Since the K–D transition involves changes in the order of the side chain, structural variations in this moiety might be expected to influence this transition but not the D–I transition, which does not involve a large change in the order of the side chains. If the disordering temperature of the side chains is higher than that at which the cores can remain stacked, the crystal will melt directly to the isotropic phase. We have undertaken a study of the effects of structural variations in the side chains of disklike molecules with the aim of developing structure–property relationships for this class of mesogen.[6,12] Addressed in terms of this simple model several approaches to rational modification of discotic thermal phase properties suggest themselves. If the K–D transition is indeed a melting or conformational disordering of the side chains, mixing different side chains should lower this transition temperature. Branching of side chains should make the regular packing more difficult, promote kinking (gauche conformations), and introduce stereoheterogeneity (for racemic side chains). All of these should have the effect of lowering the side chain melting point and thus lower T_{K-D}. At the same time the clearing temperature, since it is mainly a core unstacking process, should be little affected by these changes. Upon the basis of the examples of fatty acid melting points, it is tempting to predict that introduction of unsaturation, especially of *Z*-configuration into side chains, should also lower T_{K-D}. However, the radially oriented side chains will not pack in the same way as the parallel chains in fatty acid crystals. Thus, such an analogy is unwarranted. We report below on results, in some cases the striking success, of all the above strategies for rational modification of thermal-phase behavior of discotic liquid crystal materials.

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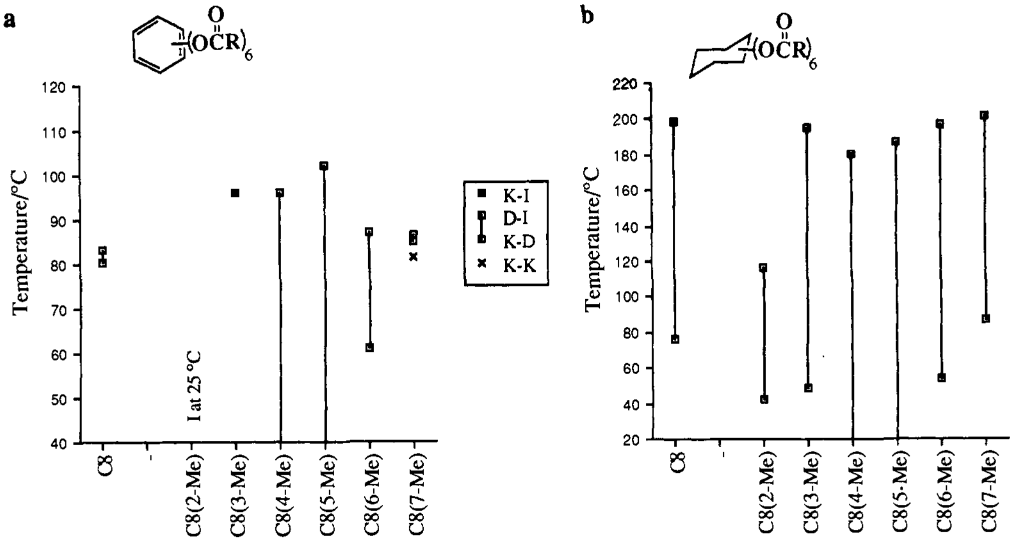

Figure 2. Thermal-phase behavior of methyl branched members of (a) **HAB-C8** series and (b) **HAChx** series.

Table III. Thermal Phase Behavior of 2,3,6,7,10,11-Hexakis(alkanoyloxy)triphenylenes with *n*-Alkyl and Branched Side Chains[a]

	transition	*T*	ΔH	ΔS
HAT-C5(5-cyPn)	K–I	161	10.5	24.1
	{I–M	130	1.1}	
	{D–I	122	8.7}	
HAB-C8[b]	K–D	66	7.5	22.1
	D–I	129	0.5	1.4
HAT-C8(2-Me)	?–I	27	6.9	23.6
HAT-C8(6-Me)	K–D	71	3.9	11.5
	D–I	159	1.4	3.3
HAT-C8(7-Me)	K–D	64	5.8	17.1
	D–I	140	0.9	2.1

[a] See Table 1 for explanation of table. [b] Compare to ref 14.

Results and Discussion

Discogens were of the following types: hexakis(alkanoyloxy)benzenes (**HAB**), 1,2,3,4,5,6-*all-trans*-hexakis(alkanoyloxy)cyclohexanes (**HAChx**), and 2,3,6,7,10,11-hexakis(alkanoyloxy)triphenylenes (**HAT**). Side-chain structure is denoted by specifying the number of carbons in the longest continuous chain, e.g., **C8** for octanoyloxy, followed by a specification of modifications to the saturated fatty acid chain in parentheses, e.g., **C8(4-Me)** for 4-methoxyoctanoyloxy and **C8(4(*E*)-ene)** for 4*E*-octenoyloxy. Thus 1,2,3,4,5,6-*all-trans*-hexakis(7-octynoyloxy)cyclohexane is designated **HAChx-C8(7-yne)**.

Branched Side Chains. Thermal-phase transitions of disklike molecules with branched side chains are given in Tables I–III.

Introduction of methyl branches in the 2-position of the octanoyloxy chain results in a destabilization of the columnar phases of the **HAB** and **HAChx** series relative to the straight chain analogues. **HAB-C8(2-Me)** is isolated as an isotropic liquid at room temperature, whereas **HAChx-C8(2-Me)** forms a mesophase with a clearing point 80 °C lower than that commonly observed for discogens of the **HAChx** series. In contrast, branching in the middle of the chain (C-4, -5, and -6, also C-3 on cyclohexane) strongly depresses the crystal–mesophase transition temperature 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 the penultimate carbon of the octanoyloxy chain has little effect. The transition temperatures of the methyloctanoyloxy members of the **HAB** and **HAChx** series are shown in Figure 2.

As a result of side chain melting point depression by branching, the 7-methyl and 4-methyl analogues of hexakis(nonanoyloxy)benzene display enantiotropic mesophases; whereas the *n*-nonanoyloxy compound itself shows only a monotropic mesophase. In analogy to the corresponding branched octanoate, the 4-methylnonanoate displays a mesophase from below room temperature to 84 °C. The 7-methylnonanoate of the **HAChx** series also displays a lower K–D transition than the corresponding straight-chain compound. But attempts to widen the mesophase ranges of **HAB-C5**, **–6**, and **-7** and **HAChx-C6** and **-7** compounds failed, possibly owing to side-chain disorder already present in the crystal state of these shorter chain discotics, see below. The high melting point of **HAChx-C6(4-Me)** compared to the behavior of its straight-chain analogue (K 68.5 D_{ho} 199.5 I)[16] is noteworthy and unexplained.

Since the depression of crystal–mesophase transition temperature could be caused by the stereoheterogeneity of the sample (with one chiral center in each of six side chains the discogens derived from racemic starting materials consist of a mixture of 13 stereoisomers) discogens with achiral 6-ethyloctanoyloxy side chains were prepared. These stereohomogeneous samples also displayed lower crystal–mesophase transitions than the *n*-alkanoyloxy analogues. The depression of the crystal-to-mesophase transition temperature caused by the 6-ethyl branch is virtually identical with that caused by the 6-methyl branch. This shows that branching is responsible for some of the depression in T_{K-D} and that stereoheterogeneity is not the sole cause of this effect.

The 5-cyclopentylpentanoyloxy side chain is of particular interest. Structurally, this side chain resembles the 6-ethyloctanoyloxy side chain with the methyl groups tied back. In the case of this side chain with a benzene core, a high melting point (130°) is obtained. This might be due to a high side-chain disordering ("melting") temperature. A discogen with this side chain would require a clearing temperature above this side-chain disordering temperature. The triphenylene analogue also exhibits an elevated melting point, 161 °C. The strategy of producing a mesophase by substitution of a core with a high unstacking (clearing) temperature succeeded in the form of the cyclohexane analogue which formed a discotic phase between an elevated T_{K-M} (143 °C) and a normal clearing temperature of 200 °C. According to the model for discotic phase formation, this side chain disorders at a temperature above that necessary to cause columns consisting of benzene cores or triphenylene to unstack. However, cyclohexane cores unstack at a higher temperature, so a mesophase is observed with this core. X-ray diffraction patterns of **HAB-C5(5-cyPn)** obtained at 30 °C (i.e., below "normal" **HAB** core unstacking temperature) and 110 °C (i.e., above expected **HAB** unstacking temperature) are identical, indicating that the cores

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Table IV. Mesophase Unit Cell Dimensions Determined by X-ray Diffraction on Unoriented Samples

	temp, °C	$a = b$, Å	c, Å
HAB-C8	82	18.4	4.6[a]
HAB-C8(4-Me)	94	19.4	4.7[a]
HAB-C8(6-Me)	77	19.2	4.9[a]

[a] The diffuse nature of this diffraction band imparts a large uncertainty in this value.

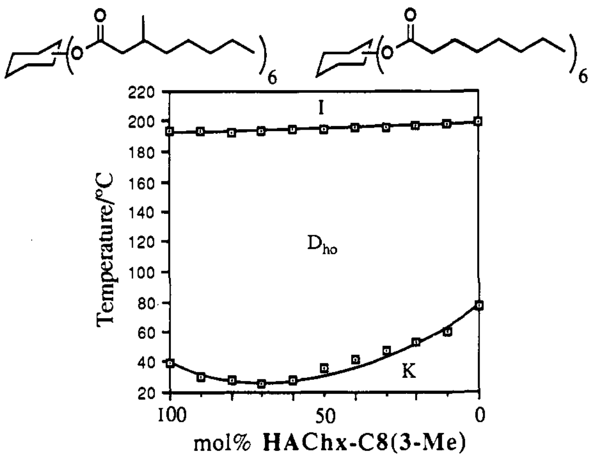

Figure 3. Phase diagram for mixtures of HAChx-C8 and HAChx-C8-(3-Me).

do not undergo a change in order in the absence of side-chain disordering.

The branched side-chain discogens form the same class of mesophase formed by the straight-chain analogues. X-ray diffraction measurements with unoriented samples (Table IV) indicate that **HAB-C8(4-Me)** and **HAB-C8(6-Me)** form a D_{hd} phase. The diffraction pattern of **HAB-C8(4-Me)** shows reflections up to the eighth order. Previously, the number of X-ray diffraction lines displayed by discotic phases has been limited to four.[18] To observe an eighth-order diffraction implies that there is considerably more long-range order in two dimensions than previously thought. Methyl branching in the side chains has the effect of slightly increasing the intercolumnar distance (a = b) (see Table IV). The stacking distance (c) between cores (ca. 4.5 Å) remains unchanged. Phase diagrams of mixtures of **HAChx-C8** and **HAChx-C8(*n*-Me)** (i.e. ***n*** = 3, Figure 3) indicate that the phases formed by the branched and unbranched compounds are the same (D_{ho}). Optical textures displayed by the branched side-chain discogens resemble those formed by the straight-chain analogues.

Homologous series of disk-like compounds with common structural features show a smooth graduation in transition temperatures. Transition temperatures of the **HAB-Cn((*n*-2)-Me)** and **HAB-Cn(4-Me)** series are shown in Figure 4. The 4-methyl compounds have higher melting or clearing points than do the straight-chain analogues. The enthalpy change for the crystal–mesophase transition of the branched compounds is lower than that for the *n*-alkanoyloxy compounds. As predicted by the simple 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 of disklike molecules (Figure 5). Stacked benzene cores in the discotic phase are separated by an average distance of 4.6 Å.[14] The effect of this destabilization is less in the case of the **HAChx** series because of the greater distance between cores along the column axis (c = ca. 4.8 Å).[18b] A number of trends for the thermal stability of discotic mesophases can be considered in reference to Figure 5. The mutual steric repulsions of bulky ester functions does not allow close packing of the benzene cores, imparting disorder along the column axis. The concept of stacking at two nearest-neighbor distances: a short core–core and a longer side-chain–side-chain distance was first discussed by Safinya et al.[19] and later by Fontes et al.[10] In general, discogens with larger cores clear at higher temperatures. One obvious exception to this is the case of the cyclohexane core which resembles the benzene core in size but which forms discotic phases which clear at ca. 200 °C compared to ca. 85 °C for the benzene series. In the case of the thicker cyclohexane core, van der Waals contact between cores can be maintained. This leads to columns with unique, well-defined, core-to-core spacing. Triphenylene cores stack with a shorter core–core spacing[18a] arising from the relief of side-chain–side-chain steric repulsions by rotation of adjacent discs around the 3-fold axis.

The depression of melting point by branching in the middle of the side chains might be due to an increase in the conformational disorder adjacent to the branch. The difference in free energy between the trans and gauche chain conformations is decreased by introduction of branch points. This has the effect of introducing a statistical bend[20] at the branch point. If the difference in free energy between the gauche and trans conformations of the side chains is small, the chains will crystallize as a mixture of the two. This bend in the side chain increases the disorder of the crystal phase and consequently lowers the entropy gain upon melting the side chain (see Tables I and II). A lower transition temperature results. An infrared spectroscopic study of the straight side-chain discogen **HAB-C8** has revealed conformational disorder about bonds to C-4 and C-6 in the crystal phase.[7,21] The gauche/trans ratio begins to grow above a crystal–crystal transition at 31° and increases continuously to the K–D transition at 81° where it increases abruptly as the side chains undergo the major disordering associated with the phase transition. The gauche/trans ratio at C-6 always exceeds that at C-4. It follows that structural changes in more disordered regions will affect the K–D transition less than changes in less disordered regions of the side chain. This is consistent with the decreasing effect of branching on the K–M transition temperature as the branch is moved out the side chain from C-4 and C-5 to C-6 and finally to C-7 where no effect is observed.

The high melting point of **HAB-C8(3-Me)**[22] might be explained by the formation of a different crystal phase from that formed by other analogues. The absence of mesophases and the high melting point for methylheptanoyloxy compounds in the benzene series and of **HAChx-C6(4-Me)** are not explained by the current treatment although it should be noted that these are branched analogues of the shortest members which display discotic mesophases in their respective series. The infrared spectra of the crytal phases of **HAB-C6** and **-C7** differ from that of **HAB-C8**.[23] These differences indicate that the **C6** and **C7** side chains contain more gauche conformations than the **C8** side chain in the crystal phase. With ^{2}H and ^{13}C NMR, Luz et al. have revealed extensive side-chain disorder in the crystal phases of **HAB-C6**.[24] The failure of branching to lower T_{K-D} for the short side-chain compounds might be explained by a high degree of disorder of *unbranched* side chains in the crystal phase.

All of the effects of branched side chains in the **HAB** and **HAChx** series are not observed in the limited number of members of the **HAT** series studied (Table III). Branching at the 6- and 7-positions of the side chains of **HAT-C8** has little effect on the

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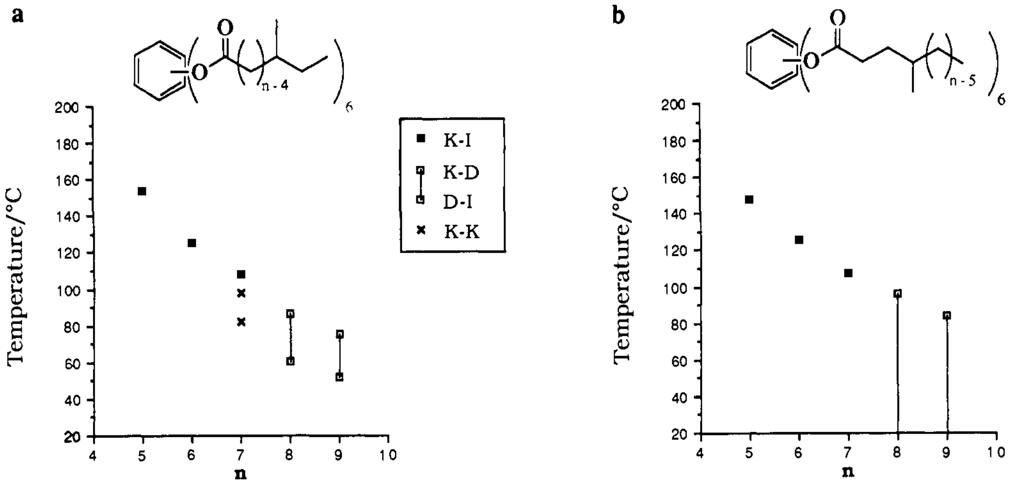

Figure 4. Thermal phase behavior of members of (a) **HAB-Cn((*n*-2)-Me)** series and (b) **HAB-Cn(4-Me)** series.

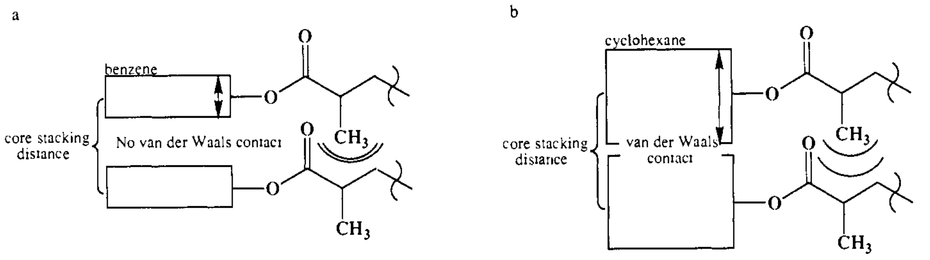

Figure 5. Stacking of disklike molecules in the mesophase. Benzene cores stack aperiodically, d_z = 4.6 Å; cyclohexanes, periodically, d_z = 4.75 Å. van der Waals contact between cores is possible in the case of cyclohexane, but not of benzene.

thermal-phase behavior. The effect of branching close to the core (i.e., at C-2) is similar to that observed for members of the other series in that **HAT-C8(2-Me)** has a low melting point. That the trends seen in the behavior of the **HAB** and **HAChx** series are not observed in the **HAT** series is not unexpected when the molecular geometry is considered. The ester linkages are less crowded on the triphenylene core, and the side chains fill proportionally less space than in the case of smaller cores. The absence of a depression of T_{K-D} by branching at C-6 in **HAT-C8** might be due to a high degree of disorder (i.e., gauche interactions in the bond pair) at this position even in the crystal phase.

Unsaturated Side Chains. The thermal-phase behavior of disclike molecules with unsaturated side chains is shown in Table V.

Unsaturation at side-chain termini of the benzene and cyclohexane discotics, **C8(7-ene)**'s and **C8(7-yne)**'s, depresses both K–D and D–I transition temperatures. Alkene functionality exerts a larger effect on K–D, while alkyne functionality does the opposite. As in the case of chain branching, effects are different for the larger triphenylene core, e.g., **HAT-C11(10-ene)**. In contrast to chain branching, the effects of introducing terminal unsaturation can be large. We have recently described depression of clearing temperatures caused by terminal bromination[12a] and heteroatom substitution.[12b] The terminal unsaturation effect takes its place with halogen and heteroatom effects on a growing list of phenomena not predicted by the simple model for discotic phase formation.

Unsaturation in the middle of the side chain generally has the effect of elevating the K–D transition temperature. Both the 4(*E*)- and 4(*Z*)-octenoyloxy side chains on the benzene core give melting points at approximately the expected unstacking temperature for the **HAB** derivatives. This observation is in accord with the concept that the side chains disorder at a slightly higher temperature than that at which the cores unstack. If this is the case, it would be expected that the side-chain disordering temperature might be observable in the **HAChx** series in which the cores unstack at a higher temperature. **HAChx-C8(4(*E*)-ene)** does form a mesophase, at 95 °C, above the **HAB** unstacking temperature, and clears at a temperature reasonable for the **HAChx** series. However, the 4*Z* analogue forms a mesophase at 36 °C, considerably below the disordering temperature of the same side chain on the benzene core. In three cases the effect of double bonds in the center of the side chain is to elevate T_{K-D} but in the fourth, **HAChx-C8(4(*Z*)-ene)**, this transition temperature is depressed. Clearing temperatures for the two **HAChx** mesogens are little changed by unsaturation in the center of the side chains.

Table V. Thermal Phase Behavior of Disklike Molecules with Unsaturated Side Chains[a]

	transition	*T*	Δ*H*	Δ*S*
HAB-C8(4(*E*)-ene)	K_{ii}–K_i	48	1.9	5.9
	K_i–I	83.5	15.8	44.3
	{I–K_{iii}	73.7	10}	
	K_{iii}–I	82.9	10	28
	{K_{iii}–K_{iv}	55.1	2}	
	{K_{iv}–K_{ii}	42.4	1}	
HAB-C8(4(*Z*)-ene)	K–I	81	5.5	15.5
HAB-C8(7-ene)	K–D	33	8.0	26.1
	D–I	70	4.0	11.7
HAB-C8(4-yne)	K–I	147	20.3	48.2
HAB-C8(7-yne)	K–D	48.4	9.5	29.6
	D–I	50.7	5.2	15.9
HAChx-C8(4(*E*)-ene)	K–D	95	7.3	19.7
	D–I	187	2.0	4.4
HAChx-C8(4(*Z*)-ene	K–D	36	4.0	12.8
	D–I	173	1.4	3.1
HAChx-C8(7-ene)	K–D	33	8.0	26.1
	D–I	191	1.8	3.9
HAChx-C8(4-yne)	K–I	199	11.7	24.8
HAChx-C8(7-yne)	K–D	69	1.6	4.7
	D–I	167	1.7	3.8
HAT-C8(7-yne)	K–I	101	4.9	13.1
HAT-C11(10-ene)	K–D	54	8.1	24.7
	D–I	79	0.2	0.5

[a] See Table I for explanation of footnotes; see Tables I–III for thermal-phase transitions for corresponding *n*-alkyl compounds.

The enthalpy of the K–D or K–I transitions of the **C8(4(*Z*)-ene)** compounds is lower than that for the corresponding *E* isomers. In terms of a model for disordering of side chains, this indicates that the *Z* isomer might be considerably disordered prior to melting

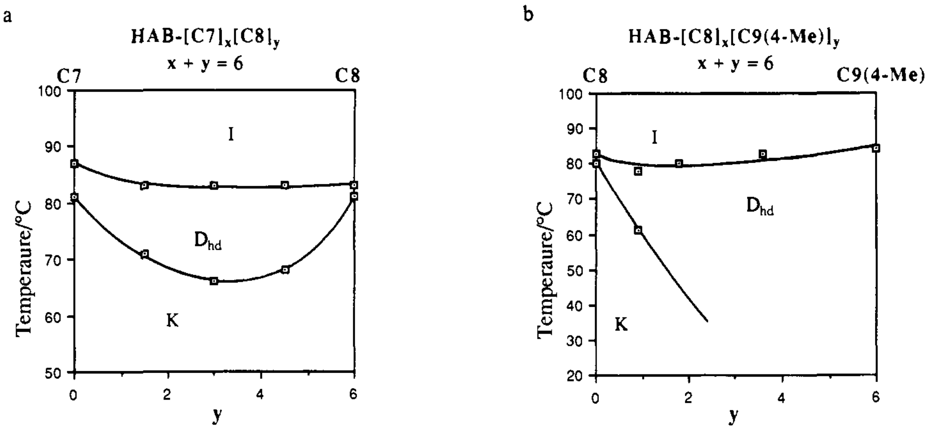

Figure 6. Phase transition curves as a function of dissimilar side-chain composition: (a) **HAB-$[C7]_x/[C8]_y$** and (b) **HAB-$[C8]_x/[C9(4\text{-}Me)]_y$**.

(or the K–D transition) compared to the *E* isomer. Although the rotation barrier about the sp^2–sp^3 bond is lower than that for the sp^3–sp^3 bond[25] and the low-energy conformation for an (*E*)-alkene has the double bond eclipsed,[26] the C-3 to C-6 unit resembles the all-trans conformation of an alkane chain, and the rigidity of this central unit seems to be the dominant effect on the flexibility of side chains with central unsaturation.

HAB-C8(4(*E*)-ene) shows interesting monotropic crystal-phase formation. The results of DSC analysis of this compound indicate (Table V) that there are a number of crystal modifications. The possibility that the K_{ii}–K_i at 48 °C is the same as that found for **HAB-C8** was investigated by mixing studies. A phase diagram for mixtures of **HAB-C8** and **HAB-C8(4(*E*)-ene)** shows a depression in the K–K transition temperature and disappearance of the former's mesophase at low content of the latter. Although this indicates that the molecules fit poorly into the other's crystal phase, the change in molecular configuration (at the K–K transition) involved in the case of **HAB-C8(4(*E*)-ene)** could still resemble that known[7] for **HAB-C8** (onset of rotational disorder adjacent C-6).

The high melting points of **HAB-C8(4-yne)** and **HAChx-C8-(4-yne)** (147 and 199 °C, respectively) are in accord with the concept that rigidity of the side chain imparts additional stability to the crystal. The data for the 4-alkenoyloxy side chains cannot be explained in such simple terms.

Discs Substituted with a Random Mixture of Two Dissimilar Side Chains. Mixing two discogens often results in broadening the mesophase range primarily by depression of the K–D transition.[14,17,27] A truly random mixture of side chains is only obtained upon incorporation of dissimilar chains on the same core. Such a random mixture is not obtained on mixing two dissimilar discogens. Increasing the random nature of the side-chain region in the crystal phase decreases the entropy gain upon formation of a mesophase. Mixtures[28] of **C7** and **C8** side chains on the benzene core affords samples with wide mesophase ranges (Figure 6a), yet extremely sharp transitions. The depression of the crystal–mesophase transition upon mixing side chains on the same core is slightly greater than that found upon mixing the two disklike molecules **HAB-C7** and **HAB-C8**.[27] Only a small fraction of **C9(4-Me)** side chain is required to bring about a large depression in the disordering temperature of the **C8** side chain on the benzene core (Figure 6b).

Conclusions

The thermal-phase behavior of disklike molecules is subject to rational control by variation of side-chain structure. Much of the data presented indicate the validity of the simple model presented in the introduction. The crystal-to-discotic phase transition involves disordering of the side chains. The temperature at which side-chain disordering takes place is lowered by incorporation of branch points. An increase in the rigidity of the chain, by virtue of unsaturation, normally increases the disordering temperature. If the disordering temperature of the side chain is higher than that at which the cores remain stacked, no mesophase is formed. The effects of side-chain structure on clearing temperatures ($T_{D\text{-}I}$) are not predicted by the simple model and are beyond the scope of this discussion.

Experimental Section

The disklike molecules were prepared by condensation of benzene,[29a] 1,2,3,4,5,6-*all-trans*-cyclohexane,[29b] and 2,3,6,7,10,11-triphenylene[29c] hexa(alcohol)s with the side-chain acyl chloride. 2-Methyloctanoic and 3-methyloctanoic acids were obtained from Dixon Fine Chemicals, Sherwood Park, Alberta, Canada. 4-Methylnonanoic acid was obtained from Lancaster Synthesis, Windham, NH. 4-Methylheptanoic and 3,7-dimethyloctanoic acid were prepared by chromic acid oxidation of the corresponding alcohols.[30] 5-Methyloctanoic acid was prepared by homologation of 4-methylheptanol via the nitrile.[31] The remaining branched alkanoic acids were prepared by the cuprate-catalyzed coupling of the secondary Grignard reagent to the appropriate ω-bromoalkanoic acid.[32] Acyl chlorides were prepared by reaction between the carboxylic acid and oxalyl chloride at room temperature. Acylations of hexahydroxybenzene[13] and -triphenylene[17] were carried out at 140 °C in the absence of solvent with an excess of the appropriate acid chloride. *scyllo*-Inositol (1,2,3,4,5,6-*all-trans*-hexahydroxycyclohexane) was acylated in trifluoroacetic acid at room temperature.[16] Samples of disklike compounds were purified by flash chromatography (on silica gel with ethyl acetate/hexanes as an eluent),[33] followed by repeated recrystallization from aqueous ethanol to constant transition temperature and gave satisfactory infrared and ^1H NMR spectra[34] and thin-layer chromatographic and combustion analyses. The thermal-phase behavior was studied by different scanning calorimetry (DSC) on a Perkin-Elmer DSC-4. Thermal transitions were reproducible during repeated heating and cooling cycles. X-ray diffraction was performed on unoriented samples in thin-walled quartz tubes (Mark-Rohrchen, FRG, from Charles Supper Co., Natick, MA) on a Siemens Kristalloflex Statton flat-film camera equipped with a brass block heating unit. Optical

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(28) The samples were prepared by heating a mixture of the two acid chlorides together with hexahydroxybenzene. Although the acid chloride feed ratio was known, some fractionation during purification might change the side-chain ratio. The ratios of the side chains determined by NMR integration (which are in accord with the feed ratio) are subject to such large uncertainties that transition temperatures are plotted against the acid chloride feed ratio in Figure 6.

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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 the disklike molecules were prepared by freeze-drying benzene solutions of the two components.

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Supplementary Material Available: ^{1}H NMR spectra, IR spectra, and combustion analysis data for all new compounds (12 pages). Ordering information is given on any current masthead page.

Surface Tension of Liquids from Molten Nitrate Mixtures to Water

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Abstract: For a long time, progress in the studies of molten salt chemistry and aqueous solution chemistry was made almost independently. Recently, salt–water systems were investigated from molten salts to water, to bridge the gap between these two fields of research, particularly concerning thermodynamic and transport properties. Another property of considerable importance to arriving at structural information on salt–water systems is the surface tension which has never been studied over the whole concentration range. Therefore, as a new step, this paper reports the results on surface tension measurements of some $AgNO_3$–$TlNO_3$–H_2O and $AgNO_3$–$TlNO_3$–$M(NO_3)_n$–H_2O systems with M = Cs, Cd, and Ca, with regard to the influence of both the water mole fraction and the temperature. By applying the Guggenheim and Adam method and the Butler equation, reasonable orders of magnitude for the values of the water mole fraction, activity, and activity coefficient in the surface phase were obtained. Moreover, it was found that the free energy of hole formation in the Fürth theory of liquids is close to the free energy of activation for the viscous flow in the Eyring equation. This result suggests that holes may be considered as fundamental structural entities in the chemistry of all solutions from molten salts to water.

1. Introduction

Compared to dilute aqueous electrolyte solutions, there is a lack of information concerning electrolyte solutions in which water plays the role of the solute, instead of the solvent. This type of solution covers a large concentration range, from the fused salts themselves to the aqueous solutions where the water mole fraction is about 0.5. In addition to technical reasons,$^{1-3}$ another one of scientific nature has attracted attention to this kind of solution. It is the suggestion,$^{2,4-10}$ made now and then, that more progress in the understanding of very concentrated aqueous solutions could come from the consideration of solutions obtained by adding water to fused salts rather than concentrating dilute aqueous solutions. As a matter of fact, this approach has proved to be fruitful in the studies of the water vapor pressure, the viscosity, and the electrical conductance of salt–water systems, over large concentration ranges.$^{10-15}$ Some of these systems have been investigated over the whole concentration range, from fused salts to water, to bridge the gap between molten salt chemistry and aqueous solution chemistry, the studies of which have advanced almost independently for a long time.

A property of considerable importance to arriving at structural information on salt–water systems is the surface tension which has never been studied over the whole concentration range. Therefore, as a new step, investigations on the surface tension of nitrate–water systems were made with regard to the influence of both the water concentration and the temperature. In the present paper, we report the results obtained in the study of electrolyte–water systems obtained by addition of water to molten salt mixtures having fixed compositions, so that they can be considered as two-component systems, i.e. salt and water. These systems are the following: $[0.515AgNO_3–0.485TlNO_3] + H_2O$ and $[0.464AgNO_3–0.436TlNO_3–0.100M(NO_3)_n] + H_2O$, with M = Cs, Cd, and Ca. The anhydrous salt system $0.515AgNO_3$–$0.485TlNO_3$ is a eutectic mixture whose freezing point is 83 °C.^{16} This mixture is convenient to establish an experimental link between molten salts and aqueous solutions, since below 100 °C it is completely miscible with water. Furthermore, around 100 °C this eutectic mixture can be doped with other nitrates, e.g. $CsNO_3$, $Cd(NO_3)_2$, and $Ca(NO_3)_2$, at mole fractions up to 0.100. The cations contained in these melts have different hydrating powers which were found to be reflected by thermodynamic and transport properties.^{2,12,14} One is then induced to examine whether the surface tension also reflects the cation hydrating power.

The water vapor pressures of these systems have been previously measured,$^{17-20}$ so that a basis exists to facilitate the exploitation

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