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Relationships Between Mesophase Temperature Range and Transition Entropies for Steroids

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An understanding of mesophase behavior requires a knowledge of the competitive forces for the stability of a mesophase relative to the corresponding isotropic liquid and the three-dimensional (normal) crystal. If the crystal is so stable so as to melt only at high temperature and/or forms readily at high temperature on cooling, formation of mesophases may be excluded or limited to a narrow temperature range.

In a series of papers from this and other laboratories, thermodynamic data have been accumulated which allow an evaluation of the tendency to form mesophases for a variety of steroid moieties. An extensive comparison may be made among specific esters for which the most abundant data are available.[1–11] Such a thermodynamic characterization has value since it has the potential of being general. Moreover, other sources of information, such as x-ray structural data, are less complete. X-ray studies as a function of temperature have been made on only a few mesophase systems. Because of the tedium involved, x-ray will likely yield to other techniques such as calorimetry as a screening and classification tool for mesophase behavior. Even with molecular models in hand, packing patterns are not obvious which can provide the subtle, yet observed, mesophase behavior of steroids.

A prime candidate for mesophase characterization is calorimetry with its ability to provide a thermodynamic basis for stability. Several generalities for mesophases have indeed resulted from apparently reliable thermodynamic studies on steroid moiety systems of good purity. Several of these have involved a systematic study of ester chain lengths attached to the same moiety. This is particularly interesting as the number and type of mesophases generally change with chain length. Figure 1 shows the general presentation of total transition entropy as a function of chain length for three homologous series.[7,8] Odd-even effects are noted in two of the three series. Both mesophase and non-mesophase forming materials show a similar trend with chain length. That is, the slope at long chain lengths corresponds closely, see Figure 1, to an increment of $R \ln 3$ in entropy for the three rotational positions available to each additional CH_2 group.[3,8] This conclusion is reassuring and provides a basis for intercomparison between the different homologous series. One approach to this comparison is to extrapolate, where possible, the data, as in Figure 1, down to zero chain length and make a comparison here among the thermodynamic stabilities of different moieties. Alternatively, comparisons may be made at a specific chain length. This is more convenient and perhaps more reliable since the actual data are obtained in this range of compositions. Among specific choices of chain length for comparison, the palmitate esters are particularly attractive. Perhaps the greatest number of compounds have been studied as this ester. It is also intermediate among esters generally studied. Moreover, mesophase formation is common

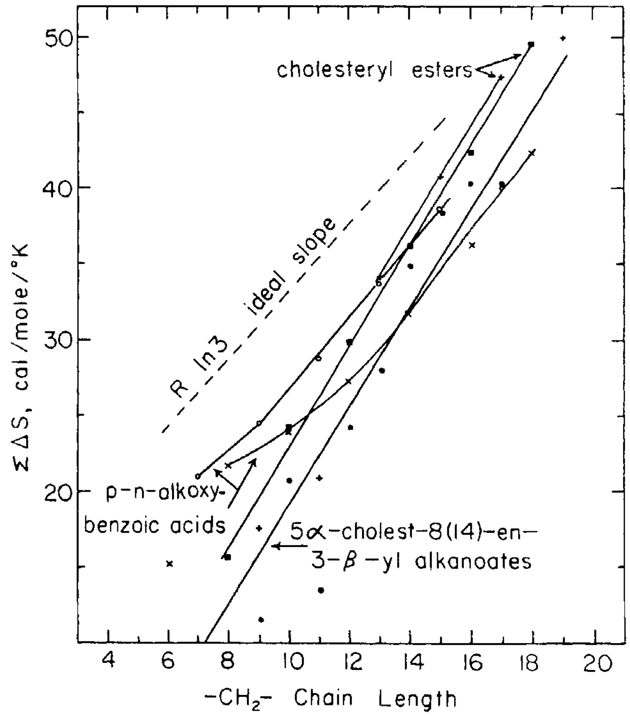

FIGURE 1 Total transition entropies for three liquid crystal series.

among palmitate esters. Table 1 lists available data on palmitate esters of steroid moieties.[1–4] These data provide an excellent possibility for analysis of mesophase formation tendency as a function of the thermodynamic properties of transition temperature and entropy.

One goal is to consider compositions that would provide the longest temperature ranges for mesophases. Comparisons are thus logically made between the properties of the stable crystals and those of the mesophases for the same compound. On this basis it may be seen, from data in Table I, that empirically there is no significant correlation of crystal transition point with the temperature range for mesophase behavior. This implies that the crystal transition point and the mesophase-isotropic transition are coupled. That is, they both are related to common structural features. The mesophase temperature range was also found not to correlate well with $\Sigma\Delta S_{\text{mesophases}}/\Delta S_{\text{crystal}}$ or $\Delta S_{\text{mesophase-isotropic}}/\Delta S_{\text{crystal}}$. In most cases, $\Delta S_{\text{crystal}}$ is only slightly less than the sum of entropies for all transitions.

The assemblage of data shown in Table I, however, does provide at least one general correlation which may be useful in predicting and designing mesophase behavior in steroid esters. Moreover, this new correlation seems to have a fundamental basis. It is also the first correlation to encompass both enantiotropic and monotropic mesophases. The new conclusion is *that the mesophase temperature range (the temperature difference between the crystal transition and the mesophase-isotropic transition) correlates well with either the heats or entropies for*:

1) the crystal melting transition,
2) all transitions up to the isotropic, or
3) the sum of all transitions.

These correlations may be seen from Table I and particularly for 1) above in Figure 2. This is the first correlation involving mesophase temperature ranges even though many synthesis programs have been conducted with the sole purpose of modifying the mesophase temperature range.

When the temperature difference is negative in these correlations, see Table I and Figure 2, the behavior is monotropic; when positive, enantiotropic. Reversible (enantiotropic) mesophases are seen to generally form when the entropy for crystal melting is less than 40 cal/mole/°K. The two compounds in Table I reportedly exhibiting a smectic-isotropic transition correlate consistently with all others which exhibit the cholesteric-isotropic transition. The deviations from Figure 2 are thus not significantly affected, at least for steroid moieties, by either the type or size (ΔS) of the mesophase-isotropic transition. Monotropic mesophase behavior is generally observed at higher entropies for crystal melting. At the highest values, ~48 cal/mole/°K,

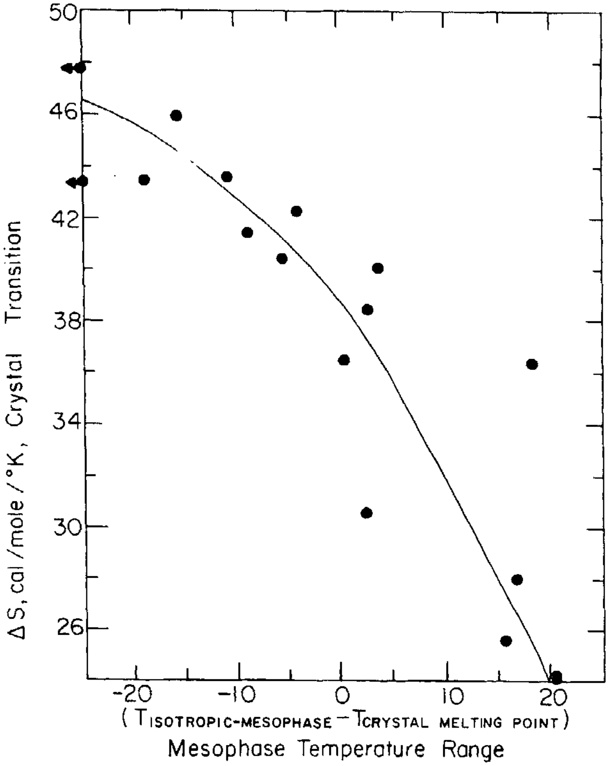

FIGURE 2 Entropy for crystal transition vs. mesophase temperature range for steroid moieties.

no mesophases are observable even at the highest rates of liquid undercooling. Rapid cooling generally retards crystal formation but mesophase formation less so, making it easier to see mesophases. At the highest crystal transition entropies, mesophase transitions are displaced into a range of at least 20°C below the crystal melting point.

The line in Figure 2 involves personal judgment. A numerical analysis suggests that the data are adequately correlated by the following linear equation:

$$\Delta S_{cr}\,(\text{cal/mole/°K}) = +37.5 - 0.50\,\Delta T\,(°\text{C}) \qquad (1)$$

These new correlations may well deserve testing at other ester chain lengths. They are not expected to hold uniformly at all chain lengths, although the evaluations are intended to interpret changes in packing of the steroid moiety. Thus the ω-phenyl palmitate esters,[5] see Table I, and one of the S-cholesteryl esters in Table I are not members of the series. In several

TABLE I

Comparison among palmitate esters

Palmitate ester	Transition entropies, cal/mole/°K				Transition temperatures, °C			Number of Mesophases	
	Sum for all transitions	Crystal transition	Mesophase-isotropic transition	Mesophases above crystal MP	a Crystal melting	b Mesophase-isotropic	b-a Temperature range	Reversible	Monotropic
Stigmasteryl[1]	47.8	47.8	—	—	102.6	—	—	0	0
ω-Phenylakanoate 5α-Cholestan-3-β-yl	46.0	46.0	1.16	1.16	65.1	49.6	−15.5	0	1
Cycloartenyl[2]	43.7	43.7	*1.15*	*1.51*	54.8	*44.6*	*−10.2*	0	1
Sitosteryl[1]	43.3	43.3	—	—	91.2	—	—	0	0
Campesteryl[1]	43.1	43.1	4.01*	4.01	91.2	72.4	−18.8	0	1
31-Norcycloartanyl[2]	43.0	30.8	12.3	21.9	67.7	70.2	+2.5	1	2
Cholesteryl carbonate[5]	42.2	42.2	0.93	(0.93)	73.9	69.2	−4.7	0	1
Cycloartanyl[2]	41.9	25.6	9.48	16.3	53.2	68.9	+15.7	2	0
Pollinastanyl[2]	41.6	41.6	1.48	3.3	58.7	50.3	−8.4	0	2
Lophenyl[1]	41.1	38.6	1.14	2.5	75.5	78.9	+3.4	1	1
Cholesteryl[3]	40.8	40.0	0.80	0.8	77.3	81.6	+4.3	1	1
5α-Cholest-8(14)-en-3-β-yl[7]	40.4	40.4	5.24*	(5.25)	73.1	67.8	−5.3	0	1
7-Dehydrocholesteryl[1]	39.3	36.2	1.05	3.1	80.5	99.3	+18.8	2	0
5α-Cholestanyl S-Alkyl Thiocarbonate	37.8	36.7	1.05	1.05	55.3	56.0	+0.7	1	1
Cholesteryl S-Alkyl Thiocarbonate[11]	~29.2	~28.0	~0.6	~1.2	47.1	63.6	+16.5	2	0
S-Cholesteryl Alkyl Thiocarbonate[6]	28.1	28.1	0.56	(1.17)	82.8	75.0	−7.8	0	2
S-Cholesteryl ω-Phenyl Alkanethioate[5]	28.0	27.6	0.34	0.34	54.6	55.3	+0.7	1	1
Thiocholesteryl[4]	25.4	24	0.35	1.4	57	87.3	+20.3	2	0

* Called smectic, all others identified as cholesteric.

( ) Monotropic mesophase entropies.

homologous series, including nematogens,[8] the mesophase temperature range increases with increasing total transition entropy. This, however, is not predominantly determined by mesophase moiety stability.

It now appears that there is the possibility of designing the desirable temperature range for mesophase existence on the basis of the intrinsic packing (entropy) of stable crystals. The correlation of transition entropies with the temperatures and stability ranges of mesophases is not perfect, yet heartening, since it is the first of its type. Yet unconsidered factors, including steroid palmitate purity, must be involved. Nonetheless, from limited additional data, and consistent with the palmitate data correlated here, the region below 20 Kcal/mole/°K for crystal melting clearly provides the region for ever longer and enantiotropic mesophase temperature ranges.

These results indicate that low thermodynamic stability for moiety packing clearly favors mesophase formation. It is also favored, however, in less pure or purposely-blended systems. This is because the van't Hoff equation, Eq. 2, generally applies only at the crystal transformation and because this transition temperature suppression is inversely α to this transition heat.

van't Hoff Equation

$$\ln N_1 = -\Delta H(T_0 - T_m)/RT_0 T_m \qquad (2)$$

N_1 is mole fraction of major component; T_0 is melting point of the pure major component, °K; T_m is the actual melting point, °K, of the mixture; ΔH is molar transition heat of the pure major component.

Equation 2 would normally be considered to result in major shifts in the mesophase transitions, because of the small heats (entropies) involved in mesophase formation, yet this is not the case. This is because many common impurities and additives for steroids actually co-mesophase so that mesophase–mesophase and mesophase–isotropic transition temperatures and heats are, in reality, insensitive to composition as indicated by phase diagrams.[9,10] Eq. 2 does apply, however, to the crystal transitions. These features will thus result in incorrectly large ranges for mesophase behavior in impure steroids. The compounds more likely to be impure would thus be those at the right of the correlation in Figure 2. Mesophases are thus more readily seen in impure systems because of the suppression of crystal transition temperatures. At the same purity, mesophases are also more readily observed with instruments that are more sensitive, more resolving and more capable of producing greater undercooling prior to crystal formation. These features may also thus be responsible for deviations in Table I and Figure 2.

The new correlations with transition entropy proposed here are also generally consistent with the number and type of mesophases that are observed. Table I shows that a greater number and more stable (enantiotropic) mesophases are formed in compounds of ever-lower crystal transition entropy.

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