

form and not in B form, because the former should have a Cotton effect of far greater magnitude than that of 8,3'-cyclonucleosides. Final clarification of this point awaits analysis by X-ray crystallography.<sup>32</sup>

For a purine  $\alpha$ -cyclonucleoside, a negative Cotton effect was observed. This is in contrast to ordinary  $\alpha$ -nucleosides, which have small positive Cotton effects.<sup>33</sup> This finding is of extreme interest because in purine cyclonucleosides the small negative Cotton effect in the parent nucleosides is converted to a large positive one. These inversions of Cotton effect in both  $\alpha$ - and  $\beta$ -cyclonucleosides suggest that the conformations of purine nucleosides in solution are not

(32) K. Tomita, unpublished results.

(33) T. R. Emerson, R. J. Swan, and T. L. V. Ulbricht, *Biochemistry*, **6**, 843 (1967).

similar to those imposed by their structures in purine cyclonucleosides with bonding to C-8.

Investigation of other properties of purine cyclonucleosides by means of physical measurement would be desirable to facilitate understanding of the conformations of purine nucleosides, especially in solution.

Purine 8-cyclonucleosides thus are interesting compounds for the elucidation of the configuration and the conformation of purine nucleosides, and they are useful as intermediates in the synthesis of various biologically interesting compounds.

*I am greatly indebted to Drs. Hiroshi Tada, Kei Muneyama, and Masakatsu Kaneko for collaboration and many suggestive discussions. I also thank Mr. Masaru Sagai, Yuji Nakahara, and Koji Tomimoto for collaboration in this work.*

## Thermodynamic Order in Mesophases<sup>1</sup>

ROGER S. PORTER

*Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01002*

EDWARD M. BARRALL II

*Chevron Research Company, Richmond, California 94802*

JULIAN F. JOHNSON

*Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268*

*Received January 23, 1968*

The melting of a crystalline substance is a familiar phase transition. The highly structured solid melts to the isotropic liquid phase at a well-defined temperature and with a characteristic heat of fusion.

In contrast, a considerable number of organic compounds—more than 3000—do not melt directly from crystalline solid to isotropic liquid.<sup>2,3</sup> Instead, the substance passes through an intermediate phase, a *mesophase*. In such a case, two phase transitions are involved: at a lower temperature, a transition from crystalline solid to mesophase, and at a higher temperature, a transition from mesophase to isotropic liquid.

The mesophase appears as a turbid liquid, and the transitions can be observed visually or by other common techniques. The term *liquid crystal* has been used interchangeably with mesophase. To a lesser extent, this state has been referred to as anisotropic or paracrystalline.<sup>2</sup>

Mesophases are ordered on a molecular level, yet possess some of the mechanical properties of liquids.

The ordered domains in mesophases contain typically about  $10^9$  molecules. However, the sense of arrangement of the molecules is not the same in all mesophases. Three basic types are recognized: nematic, smectic, and cholesteric mesophases. A single compound can exhibit more than one mesophase.

Figure 1 illustrates the general structural features of the three mesophases. The nematic type is the simplest. In pure compounds, *e.g.*, *p*-azoxyanisole, the nematic mesophase is thought to consist of bundles of rodlike structures. The only structural restriction in nematic mesophases is that the molecules are parallel or nearly parallel within a bundle.

In the smectic mesophase, molecules are arranged side by side in a series of stratified layers,<sup>2a</sup> *e.g.*, diethyl *p,p'*-azoxydibenzoate. Molecules in the layers may be arranged in a regular or random side-by-side spacing. The long axes of the molecules are parallel to one another and essentially perpendicular to the base plane of the layer. The layer can be one or more molecules thick. In general, the smectic mesophase has greater order than the nematic.

The third type is the cholesteric mesophase; it is formed principally by derivatives of cholesterol, *e.g.*, cholesteryl benzoate, but not by cholesterol itself.

(1) Part XVI of a series on Order and Flow of Liquid Crystals.

(2) (a) G. H. Brown and W. G. Shaw, *Chem. Rev.*, **57**, 1049 (1957);

(b) J. L. Ferguson, *Sci. Am.*, **211**, 76 (1964).

(3) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y., 1962.

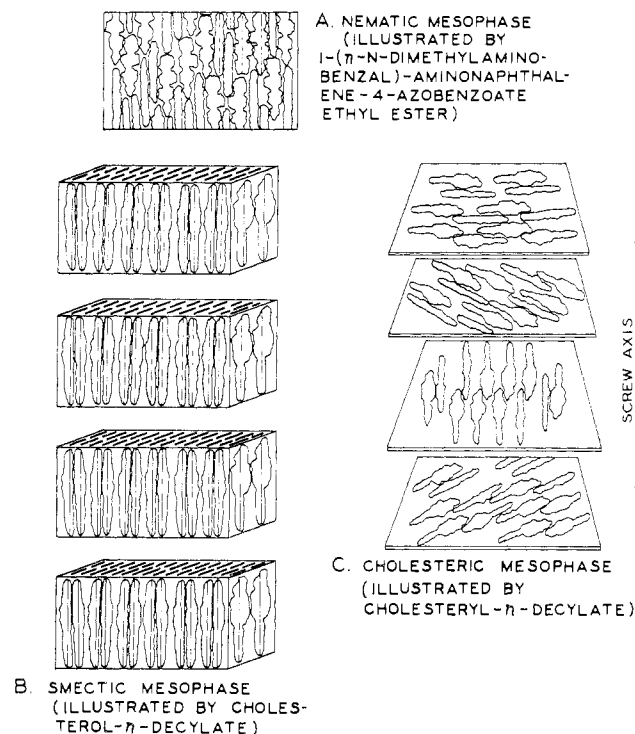


Figure 1.

The cholesteric mesophase resembles the smectic mesophase in that molecules are arranged in layers. Within each layer, however, the parallel arrangement of molecules is reminiscent of the nematic mesophase. The cholesteric layers are thin with the long axis of molecules parallel to the plane of the layers. A screw axis runs through the layers.<sup>3</sup>

A relatively new focus in mesophase research is calorimetric study of the phase transitions. From the molar heats of transition,  $q$ , the entropy change of transition is calculated from the familiar relationship,  $\Delta S = q/T$ , where  $T$  is the absolute temperature. Only about a dozen mesophase-forming compounds had been subjected to such calorimetric study prior to 1960, but now more than 50 have been examined. The recent work has been carried out principally at Chevron Research Co., Richmond, Calif.; Fort Belvoir, Va.; the University of Massachusetts; and Martin-Luther University, Halle, Wittenberg, East Germany. The latter university has had a continuing program in mesophase research since the 19th century.

The purpose of this paper is to present and examine the thermodynamics of mesophase transitions exhibited by pure compounds. Lyotropic mesophases, *i.e.*, those formed in solution, are not considered because virtually no calorimetry is available for these systems. Transition data have been reported on mesophases formed by pure compounds in several homologous series. Within each series, the length of a hydrocarbon chain bonded to some basic mesophase-forming structural unit is varied. Such series can provide an insight into mesophase behavior since the most significant regularities in transition entropies and temperatures are

provided by the normal paraffins and their derivatives.

We shall be interested in two "events" in connection with any mesophase: the solid-mesophase transition which occurs at a lower transition temperature, and the mesophase-isotropic liquid transition which occurs at a higher transition temperature. It is a fact that the heat of the solid-mesophase transition is generally much larger than that of the mesophase-isotropic transition, and the two "events" are therefore sometimes referred to as the major and minor calorimetric events, respectively.

### Calorimetric Results

In 1964 Arnold initiated a concerted program on mesophase calorimetry.<sup>4-8</sup> His method of measurement has been adiabatic calorimetry. The precision of his transition heat measurements has been suggested to be 0.2%. However, variations in calculation method can lead to much larger uncertainties.<sup>4-8</sup> Barrall, *et al.*, also in 1964, began transition heat studies on mesophases.<sup>9-13</sup> Their methods have been differential thermal analysis and differential scanning calorimetry. The precision of these methods is 2-10%, with uncertainty decreasing as the heat of transition increases. These techniques provide transition temperatures as well as transition heats. Temperatures can be measured to better than 0.1° and are reliable to better than 1.0°. All types of mesophase-isotropic transitions exhibit prominent post- and pretransitional effects in terms of specific heat and specific volume as well as other properties.

**A. *p,p'*-Di(*n*-alkoxy)azoxybenzenes.** 1. *Mesophase-Isotropic Transition.* Arnold has presented a consistent set of data on this series. New correlations, based on these data, are shown in Figure 2. An odd-even effect is evident: if lines had been drawn connecting successive points, a saw-tooth-shaped plot would have resulted. Odd-even effects have been encountered previously in the transition temperatures for mesophases in several series containing *n*-alkoxy groups, with the odd-even curves merging at high molecular weight.<sup>14</sup> The novelty of Figure 2 is that a pronounced odd-even effect is observed in calorimetric data. It is to be noted that the curves for odd and even members merge at about  $C_8$ . In the region of the unified curves, the transition heat ascends steeply

(4) H. Arnold, *Z. Physik. Chem. (Leipzig)*, **225**, 45 (1964).

(5) H. Arnold, *Z. Chem.*, **4**, 211 (1964).

(6) H. Arnold, *Z. Physik. Chem. (Leipzig)*, **226**, 146 (1964).

(7) H. Arnold, *Mol. Crystals*, **2**, 63 (1966).

(8) H. Arnold and P. Roediger, *Z. Physik. Chem. (Leipzig)*, **231**, 407 (1966).

(9) E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.*, **68**, 2810 (1964).

(10) E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Chromatog.*, **21**, 392 (1966).

(11) E. M. Barrall II, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.*, **70**, 385 (1966).

(12) E. M. Barrall II, R. S. Porter, and J. F. Johnson, *ibid.*, **71**, 1224 (1967).

(13) E. M. Barrall II, Presented at the Second International Conference on Thermal Analysis, Holy Cross College, Worcester, Mass., Aug 18-23, 1968.

(14) J. S. Dave and P. R. Pater, *J. Mol. Crystals*, **2**, 103, 115 (1966).

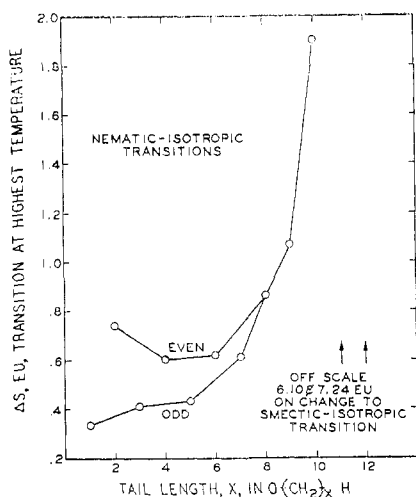


Figure 2. Transition entropies for nematic-isotropic transitions of  $p,p'$ -di( $n$ -alkoxy)azoxybenzenes.

as a function of molecular weight. Indeed, this is just the region where the nature of the phase transition has been identified by optical observations as changing from nematic-isotropic to smectic-isotropic. For one member of the series,  $C_7$ , an inconsistency in calorimetric values exists in the literature.<sup>5-7</sup>

2. *Crystal-Mesophase Transition.* There is no significant odd-even effect for the entropy of this transition. It appears likely that changes in the ether-azoxy dipole interaction are responsible for changes in transition entropy in this major thermal event (*cf.* Figures 2 and 3). Arnold, in a block diagram, has suggested that the total order in mesophases increases with molecular weight except for minor odd-even effects at low molecular weight. The upward trend in Figure 2 is consistent with this interpretation. The magnitude of the effect is, however, relatively small, and it is difficult to recognize in the transition entropies associated with the major calorimetric event. This is evident in Figure 3, which shows the crystal-mesophase transition entropy and temperature as a function of molecular weight. Prominent in Figure 3 is a trend at lower chain lengths toward a minimum transition entropy at  $C_5$  and then a sharp rise to  $C_6$ . From  $C_6$  to  $C_{10}$  both the transition temperature and the entropy are relatively constant. In this range, if increasing chain length causes any change in the entropy of the mesophase, a compensating change in the entropy of the crystal must occur. The  $C_9$ - $C_{12}$  compounds can be considered a series with the transition entropy increasing modestly but regularly with molecular weight. The incremental entropy is likely due to liberated motions of the hydrocarbon tail.

3. *Mesophase-Mesophase Transition.* Two mesophases, a smectic at lower temperature and a nematic at higher temperature, are formed in this series by members with terminal groups in the range from heptoxy through decyloxy. This is the region where there is a plateau in the total transition entropy change with molecular weight. The phenomenon of constant

transition entropy and the appearance of an intermediate mesophase are clearly associated. The responsible molecular mechanism cannot be determined with existing information.

**B. Esters of Cholesterol.** Gray has provided a systematic study of transition temperatures for mesophases in aliphatic esters of cholesterol.<sup>15</sup> Transition temperatures have been measured by differential thermal analysis<sup>11</sup> as well as by other means.<sup>3,15</sup> The first six members of the series exhibit only a cholesteric mesophase. Cholesteryl heptanoate and the higher members may exhibit two mesophases: a smectic mesophase coverts to a cholesteric type at higher temperature. Odd-even carbon number effects are observed for the mesophase-isotropic transition temperature. The esters with an uneven number of carbon atoms in the alkyl chain give rise to the uppermost of two curves. This feature has been reported in several other series involving a change in hydrocarbon tail length.<sup>8,14,15</sup>

Only recently have calorimetric values become available for the series of aliphatic esters of cholesterol.<sup>12</sup> Progress has also been reported in calorimetric studies on other series of cholesterol derivatives such as the carbonates and  $\omega$ -phenyl alkanates and the corresponding thioesters and carbonates.<sup>16</sup>

1. *Mesophase-Isotropic Transition.* In the available data (Figure 4),<sup>12,13,17,18</sup> this transition shows an increase in entropy with increasing molecular weight with a sharp break at an  $x$  of 7-8 for  $(CH_2)_x$ . A regular relationship exists at the  $C_9$  acid ester and above. This suggests that the same kind of change in organization and motion occurs at this transition for the higher esters and that the transition involves, at least in part, the "tail" of the ester. At the lowest molecular weights, the transition entropy is essentially independent of tail length. This may mean that the short tails have as much flexibility, or inflexibility, in the mesophase as they do in the isotropic liquid, and that the transition entropies are largely concerned with freeing the cholesteryl moieties from each other. The value, 0.35 eu, obtained for cholesteryl benzoate is near the lower limit of the entropy curve for the aliphatic esters; *cf.* Figure 4.<sup>11</sup> This supports the view that changes in the relationships between the cholesteryl moieties represent the main contribution to the transition entropy, and that there is little or no contribution due to the flexure of short hydrocarbon tails. The unsaturated oleate ester transition entropy is three times that for the palmitate and stearate esters (although a lower value has been obtained by Gray<sup>19</sup>). An alternate or supplemental process may be involved here; the less flexible oleyl group may change the

(15) G. W. Gray, *J. Chem. Soc.*, 3733 (1956).

(16) R. D. Ennulat, Presented at the Second International Conference on Liquid Crystals, Kent State University, Kent, Ohio, Aug 1968.

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(18) M. Leclercq, J. Billard, and J. Jacques, *Compt. Rend.*, **264**, Ser. C, 1789 (1967).

(19) A. P. Gray, *Thermal Analysis Newsletter*, No. 4, Perkin-Elmer Corp., Norwalk, Conn.

spacings between molecules in the mesophase.

A comparison may be made between the mesophase-isotropic transition in this series and that in other series. The azoxybenzene derivatives are comparable only at low molecular weights where the transition is of the nematic-isotropic type. In this region, the transition entropies for the odd azoxybenzene derivatives increase at a comparable rate and over the same range, 0.3 to  $-0.8$  eu, as do those in the ester series. This suggests that a similar process is involved in the transition in both series and that contributions due to the differences in the basic molecular frameworks or to the difference between an ester linkage and an ether linkage are small. The lower esters do not show odd-even effects in mesophase-isotropic transition entropies as do the azoxybenzene derivatives (*cf.* Figures 3 and 4).

2. *Crystal-Mesophase Transition.* There are irregularities and perhaps minor odd-even effects in entropy changes with molecular weight for the low molecular weight members of the series (see Figure 4). Figure 4 shows that there is an abrupt break in the plots of transition entropy change against molecular weight at the same composition for the crystal-mesophase, mesophase-isotropic, and total transition entropy. It is important to note that this is just the composition where other measurements have indicated the appearance of a second mesophase for the  $C_9$  and higher aliphatic esters.<sup>15</sup>

Significantly, at long chain lengths, the transition entropy increases regularly and prominently. The isotropic transition entropy also starts a regular increase in the same molecular weight range. However, the increase in isotropic transition entropy cannot account for the large change in the total transition entropy. This means that the lower temperature transitions are also affected by the hydrocarbon tail at long tail lengths. It is presently difficult to envision how the hydrocarbon tail can influence the packing of cholesteryl groups. Interstitial positioning may be possible.

The interrelationship of the two mesophase transitions for this series is revealed by a new empirical correlation. The transition at highest temperature is  $\sim 2\%$  of the total transition entropy for each of the measured esters exhibiting both transitions. This remarkably strong empirical correlation demands the conclusion that the two mesophase transitions are phenomenologically interrelated.

The conclusions drawn for the entropies of the lowest temperature transition also generally hold for the sum of transition entropies. This is because the greater part of the total entropy gain between solid and isotropic liquid, 98%, is at the lower transition temperature.

3. *Mesophase-Mesophase Transition.* Two esters, the *n*-propionate and the myristate, exhibit three reversible transitions; the intermediate transition involves an increase in entropy of about 0.2 eu. The intermediate transition involves a heat or liberation of motion that is part of the lowest temperature

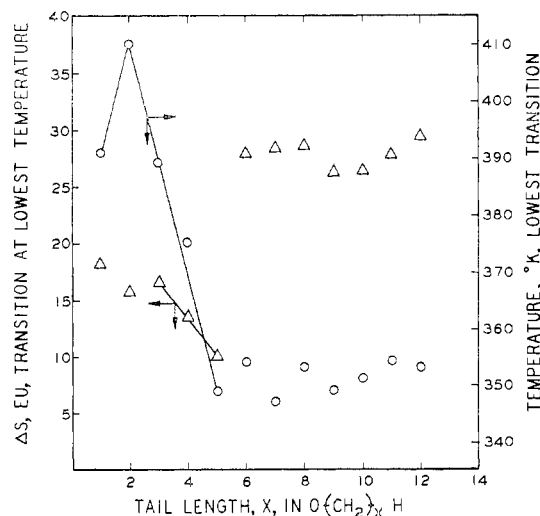


Figure 3. Transition entropies (triangles; left scale) and temperatures (circles; right scale) for crystal-mesophase transitions of *p,p'*-di(*n*-alkoxy)azoxybenzenes.

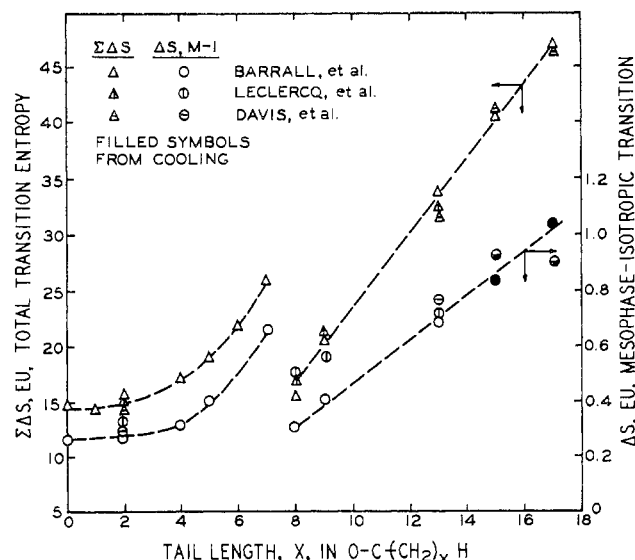


Figure 4. Total crystal-isotropic liquid transition entropies (triangles; left scale) and mesophase-isotropic transition entropies (circles; right scale) for aliphatic esters of cholesterol.

transition in the other esters. This is shown by the fact that the entropies for the mesophase-isotropic transitions for these two compounds fall smoothly into a series with other esters not exhibiting this intermediate mesophase; see Figure 4. More calorimetric information is needed on intermediate mesophase transitions which are exhibited principally by the higher members of the series.

## Discussion

A. *Mesophase Identification.* *p*-Azoxyanisole, the most widely studied of all mesophase compounds, and diethyl *p,p'*-azoxydibenzoate, a close structural relative, offer an interesting contrast. The latter forms only a smectic, the former only a nematic mesophase.

Their transition entropies provide an incisive measure of differences between smectic and nematic mesophases. The total of the two first-order transition entropies for *p*-azoxyanisole is 19.5 eu vs. 15.5 eu for the ester. Entropies for the mesophase-isotropic transition are in reverse order, 0.43 vs. 3.2 eu.<sup>20</sup> The nematic-isotropic transition thus represents 2.2% of the total entropy gain at the two transitions, in contrast to 20% for the smectic-isotropic transition of the ester. This indicates a difference, by a factor of nearly 10, in fractional order change between nematic-isotropic and smectic-isotropic transitions. Terminal moieties may thus affect molecular association in mesophases more than the central group—which is the same for this pair—in determining mesophase structure and stability.

**B. Long Hydrocarbon Tails.** Mesophase-isotropic transitions may be compared among compounds containing long hydrocarbon tails. These include the several series discussed previously, the interesting recent work by Hebert on the *p*-*n*-alkoxybenzoic acids, and data on the compound di-*n*-dodecyl *p,p'*-azoxy- $\alpha$ -methylcinnamate.<sup>8</sup> This compound and the *p,p'*-di(*n*-alkoxy)azoxybenzene derivative of equivalent alkyl chain length have high isotropic transition entropies of 5.8 and 7.2 eu, and both are said to be smectic-isotropic transitions.<sup>7,8</sup> Both compounds contain two dodecyl groups per molecule, yet the isotropic transition entropy is well over twice that for the C<sub>12</sub> derivatives in soaps and cholesteryl esters which have mesophase-isotropic transition entropies of 1.4 and 0.5 eu, respectively (the latter value is an interpolation).<sup>21</sup> These results are consistent with the calorimetric distinction made above for discriminating between smectic and nematic mesophases.

Mesophase systems are more like liquids than crystals since by far the greatest entropy change occurs at the lower transition temperature. Bondi has suggested that the major calorimetric event will occur in the temperature range where melting would be expected for a comparable compound which exhibits no mesophase.<sup>22</sup> The highest temperature transition entropy is usually the smallest. It is also the most readily interpreted. A lower limit for transition entropy may represent the contribution of the basic structural unit exclusive of pendant groups. In the various series, this would be the groups  $-\text{OC}_6\text{H}_4\text{NO}=\text{NC}_6\text{H}_4\text{O}-$ , cholesteryloxy, and  $-\text{COO}^-\text{Na}^+$ .<sup>21</sup>

**C. Partitioning of Order and Mesophase Classification.** The basic mesophase types can be identified empirically by the fraction of total transitional entropy which is associated with the mesophase-isotropic transition. This fractional entropy for smectic mesophases is some five to ten times that for the transitions of nematic and cholesteric mesophases. The latter

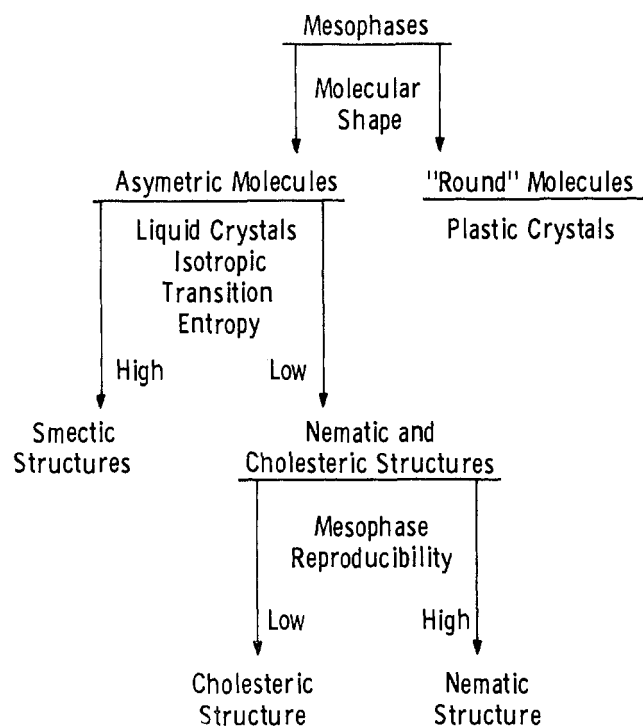


Figure 5. Classification of mesophases by composition and thermodynamics.

group also includes soaps which have heretofore been grouped with smectic mesophases.<sup>21</sup> An abrupt increase in the isotropic transition entropy is noted on going from the nematic to the smectic type of mesophase within the homologous series *p,p'*-di(*n*-alkoxy)azoxybenzenes. Also noted above is the large calorimetric difference between the similar compounds, *p*-azoxyanisole<sup>6</sup> and diethyl *p,p'*-azoxydibenzoate,<sup>20</sup> the former exhibiting only a nematic mesophase and the latter only a smectic. A schematic classification of mesophases by composition and thermodynamics is given in Figure 5. This new scheme may be compared with the classification by thermal stability range given by Brown and Shaw, in which phase identifications are based on optical techniques.<sup>2a,3</sup> There are distinct limitations to each of these schemes. A more definitive classification, which can also treat orientation, can be based on radial distribution functions. This approach is being developed by Professor R. S. Stein of the University of Massachusetts.

Smectic mesophases may be considered as part of a larger class of systems referred to as plastic crystals. Plastic crystals are "soft" crystals having low yield stresses, measurable viscosities, and involving molecules which have freedom in the crystal lattice, that is, freedom to rotate or vibrate in place.<sup>23,24</sup> Examples are found among spherical or symmetrical molecules (with the latter including normal paraffins). Among other features, plastic crystals (a) have low isotropic

(20) M. E. Spaght, S. B. Thomas, and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

(21) R. D. Vold, *J. Am. Chem. Soc.*, **63**, 2915 (1941).

(22) A. Bondi, *Chem. Rev.*, **67**, 565 (1967).

(23) J. G. Aston in "Physics and Chemistry of the Organic Solid State," D. Fox and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 9.

(24) E. F. Westrum, Jr., and J. P. McCullough, Chapter 1 in ref 23.

transition heats, (b) are glasslike and tacky, and (c) exhibit one or more transformations below the isotropic transition. Plastic crystals are generally classified as having isotropic transition entropies of less than 5 cal/mol.<sup>23-25</sup> It is now known that nearly all mesophase-isotropic transition entropies are in this range.

In contrast to plastic crystals, movement of molecular centers of gravity probably occurs within nematic and cholesteric mesophases. The isotropic transition in plastic crystals involves breaking of residual crystal lattice bonds. In the cases of nematic and perhaps cholesteric mesophases, the isotropic transition may likely involve liberation of restricted internal motions.

Compounds which form a nematic or a cholesteric mesophase are empirically equivalent and indistinguishable on the basis of the transition entropy criterion. This is contrary to the conclusions of Gray, based on microscopic observations, that cholesteric mesophases are more similar to smectic than to nematic.<sup>15</sup> The isotropic transition heat is small for cholesteryl esters. It is a remarkably constant percentage of the total transition heat,  $\sim 2\%$  for all esters studied.

This new criterion also holds for esters exhibiting only monotropic transitions<sup>26</sup> between the mesophase and the isotropic liquid. These include the formate, palmitate, and stearate esters of cholesterol. For each of the esters, the isotropic transition entropy is about 2.0% of the total transition entropy. This fraction may be compared with the transition entropy for the nematic-type mesophase. For a wide range of structural compositions, the per cent transition entropy at the mesophase-isotropic transition is in the range 1.2-4.5%. For the *p,p'*-di(*n*-alkoxy)azoxybenzenes (up to decyloxy), the range is from 1.8 to 4.5%. The lowest value, as reported by Arnold, is for the lowest member of the series, *p*-azoxyanisole. These values are all similar to the 2.0% found for cholesteric-isotropic transitions. Thus, a minimum fractional transition entropy for mesophase formation is suggested. This limit may also be considered a minimum criterion for stable structure formation in liquids. The results signify a constant partitioning of order between phases, approximately independent of composition. This concept covers mesophase transition temperatures which vary by over 200°. A constant partitioning of order between transitions also holds for the series of normal paraffins.

Friedel pointed out that there is no known case of a compound that gives both a cholesteric and a nematic mesophase.<sup>27</sup> He concluded, from other reasoning, that the cholesteric mesophase should be considered similar to and indeed a special type of nematic mesophase. From nuclear magnetic resonance data it has

been concluded that the nematic mesophase is but a special case of the cholesteric type; in the former the pitch of the helical structure is said to be infinite.<sup>28</sup> Among cholesteric- and nematic-type mesophases, a distinction may sometimes be made on the basis of reproducibility of phase formation. Compounds which form nematic mesophases do so independent of whether the compound is crystallized from the melt or from solution. Heats and temperatures for nematic mesophase formation are also generally independent of whether measurements are made by heating or cooling. In contrast, many compounds which form cholesteric mesophases show phase transitions which depend on previous history of temperature and solvent treatment. Gray has pointed out other irreversible features, observed optically, which distinguish the cholesteric mesophase.<sup>15</sup>

## Conclusions

In general, nematic and cholesteric mesophases exhibit small entropies of first-order transition to the isotropic liquid. Calorimetry provides quantitative information on mesophase stability and a basis for an independent method of identifying and classifying the fundamental mesophase types.

Entropies summed over the several mesophase transitions for any compound also offer a basis for comparison. This is because the transition temperatures for a given compound are relatively close on an absolute temperature scale so that specific heat contributions are minor. The fraction of total transition entropy at nematic-isotropic transitions exhibits a common minimum,  $\sim 2\%$ , for many derivatives. This value agrees remarkably well with the common fractional transition entropy for cholesteric-isotropic transitions. In this way, a minimum thermodynamic requirement is suggested for mesophase formation or, in general, the formation of structures in liquids. The reason that this minimum takes the form of a fraction rather than an absolute value is unknown.

Calorimetrically, smectic liquid crystals differ markedly from the cholesteric and nematic types. Smectic-isotropic transition heats are generally five to ten times higher than for the other two types of mesophase-isotropic transitions. This higher order indicates that smectic mesophases are perhaps more closely akin to plastic crystals than to nematic and cholesteric mesophases.

The sum of all transition entropies for each member in the several homologous mesophase series shows that total order increases with molecular weight. There may be considerable variation, however, between adjacent members in a series.

*This survey was supported in part by a grant from the National Institutes of Health.*

(25) A. R. Ubbelohde, *Trans. Faraday Soc.*, **34**, 292 (1938).

(26) Monotropic transitions are those observed only on cooling the sample and not on heating.

(27) G. Friedel, *Ann. Phys.*, **18**, 273 (1922).

(28) E. Sackmann, S. Merboom, and L. J. Snyder, *J. Am. Chem. Soc.*, **89**, 5981 (1967).